



Technical Support Document for Best Management Practices for Spent Pulping Liquor Management, Spill Prevention and Control

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**TECHNICAL SUPPORT DOCUMENT
FOR
BEST MANAGEMENT PRACTICES FOR
SPENT PULPING LIQUOR MANAGEMENT, SPILL PREVENTION, AND CONTROL**

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SPECIALIZED DEFINITIONS

- (1) *Action Level:* A daily pollutant loading that when exceeded triggers investigative or corrective action. Mills determine action levels by a statistical analysis of six-months of daily measurements collected at the mill. For example, the lower action level may be the 75th percentile of the running seven-day averages (that value exceeded by 25 percent of the running seven-day averages) and the upper action level may be the 90th percentile of the running seven-day averages (that value exceeded by 10 percent of the running seven-day averages).
- (2) *Equipment Items in Spent Pulping Liquor, Soap, and Turpentine Service:* Any process vessel, storage tank, pumping system, evaporator, heat exchanger, recovery furnace or boiler, pipeline, valve, fitting, or other device that contains, processes, transports, or comes into contact with spent pulping liquor, soap, or turpentine. Sometimes referred to as “equipment items.”
- (3) *Immediate Process Area:* The location at the mill where pulping, screening, knotting, pulp washing, pulping liquor concentration, pulping liquor processing, and chemical recovery facilities are located, generally the battery limits of the aforementioned processes. “Immediate process area” includes spent pulping liquor storage and spill control tanks located at the mill, whether or not they are located in the immediate process area.
- (4) *Intentional Diversion:* The planned removal of spent pulping liquor, soap, or turpentine from equipment items in spent pulping liquor, soap, or turpentine service by the mill for any purpose including, but not limited to, maintenance, grade changes, or process shutdowns.
- (5) *Mill:* The owner or operator of a direct or indirect discharging pulp, paper, or paperboard manufacturing facility.
- (6) *Senior Technical Manager:* The person designated by the mill manager to review the BMP Plan. The senior technical manager shall be the chief engineer at the mill, the manager of pulping and chemical recovery operations, or other such responsible person designated by the mill manager who has knowledge of and responsibility for pulping and chemical recovery operations.
- (7) *Soap:* The product of reaction between the alkali in kraft pulping liquor and fatty acid portions of the wood, which precipitate out when water is evaporated from the spent pulping liquor.

- (8) *Spent Pulping Liquor*: For kraft and soda mills “*spent pulping liquor*” means black liquor that is used, generated, stored, or processed at any point in the pulping and chemical recovery processes. For sulfite mills “*spent pulping liquor*” means any intermediate, final, or used chemical solution that is used, generated, stored, or processed at any point in the sulfite pulping and chemical recovery processes (e.g., ammonium, calcium, magnesium, and sodium base sulfite liquors).
- (9) *Turpentine*: A mixture of terpenes, principally pinene, obtained by the steam distillation of pine gum recovered from the condensation of digester relief gases from the cooking of softwoods by the kraft pulping process. Sometimes referred to as *sulfate turpentine*.

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1.0 INTRODUCTION

This document presents information for Best Management Practices (BMPs) for bleached papergrade kraft and soda, and papergrade sulfite mills. EPA promulgated these BMPs pursuant to section 304(e), section 307(b) and (c), section 402(a), and section 501(a) of the Clean Water Act (CWA) for mills subject to 40 CFR Part 430, Subpart B - Bleached Papergrade Kraft and Soda, and Subpart E - Papergrade Sulfite.

The BMPs establish controls that will reduce the release of toxic, conventional, and non-conventional pollutants to navigable waters. The principal objective of the BMPs is to prevent losses and spills of spent pulping liquor (also referred to as "black liquor" at kraft mills) from equipment items in pulping liquor service; the secondary objective is to contain, collect, and recover, or otherwise control, spills, losses and intentional liquor diversions that do occur. The BMPs also apply to pulping by-products, such as turpentine and soap, for mills that process these items.

Economic operation of kraft and sulfite pulping processes is predicated on the recovery of inorganic pulping liquor chemicals and energy from the organic material dissolved from the wood supply during the pulping processes. However, the nature of pulp screening, washing and pulping liquor recovery systems is such that losses of spent pulping liquors (e.g., kraft black liquor and sulfite red liquor) are routine. Liquor is lost from seals on brownstock washers, pumps and valves in liquor service, knotters and screens, sewerage evaporator boil-out solutions, and other intentional liquor diversions during maintenance, startups and shutdowns. Spent pulping liquor is also lost in spills resulting from process upsets, tank overflows, mechanical breakdowns, operator errors, and construction activities. Research into spill incidents reported through EPA's Emergency Response Notification System shows that only a few pulping liquor

spills have resulted from catastrophic failures of bulk liquor storage tanks. Mechanical failure was cited in 45% of reported liquor spills, human error in 20%, tank overfilling in 16%, and intentional diversions in 4%. The cause of 13% of the spills was reported as unknown. In addition, mill operators intentionally divert pulping liquors from the process during certain maintenance operations and during process start-ups and shut downs (20).

Liquor losses and spills not only adversely affect economic operation of the pulping process but can also adversely affect wastewater treatment system operations and lead to increased effluent discharges of conventional and toxic pollutants. These wastewater treatment systems operate most effectively when influent variability is minimized. Thus, achievement of minimum effluent discharges is only possible at mills where routine liquor losses, intentional liquor diversions, and unintentional liquor spills are effectively controlled.

These BMPs focus on controlling spent pulping liquor losses and intentional liquor diversions from chemical pulp mills to control toxic pollutants for the following reasons:

- (1) Spent pulping liquor spills and intentional liquor diversions are a principal cause of upsets and loss of efficiency in biological wastewater treatment systems that are nearly universally used for the treatment of chemical pulp mill wastewaters. The resulting interference with biological treatment system operations can lead to pass-through of conventional pollutants, priority pollutants, and non-conventional pollutants that would otherwise be treated or removed.
- (2) Losses of pulping liquor are a significant contribution to untreated wastewater loadings and discharge loadings of color, oxygen-demanding substances, and non-chlorinated toxic compounds from chemical pulp mills.
- (3) Prevention and control of spent pulping liquor losses is a form of pollution prevention that will result in less demand for pulping liquor make-up chemicals; increased energy efficiency through recovery of liquor solids; more effective and less costly wastewater treatment system operations; and reduced formation of wastewater treatment sludges.

- (4) Control of spent pulping liquor losses will result in incidental reductions in atmospheric emissions of Total Reduced Sulfur (TRS) compounds from kraft mills and volatile hazardous air pollutants (HAPs) from all chemical pulp mills implementing these BMPs.

This document presents information on BMPs for controlling losses of spent pulping liquor, soap and turpentine. Section 2.0 summarizes EPA's legal authority to promulgate BMP requirements. Wood composition is described in Section 3.0. The major chemical pulping and recovery processes are briefly reviewed in Section 4.0. The chemical composition and toxicity of pulping liquors, soap and turpentine are described in Section 5.0. Sources of pulping liquor losses are described in Section 6.0. Current industry practices regarding spent pulping liquor management, spill prevention, and control are reviewed in Section 7.0, along with discussion of spill containment measures for soap and turpentine. The BMP requirements are described in Section 8.0. Estimated costs, effluent reduction benefits, and current industry status with respect to implementing BMPs are presented in Section 9.0.

2.0 LEGAL AUTHORITY

In the BMP regulation codified at 40 CFR 430.03, EPA is requiring mills with pulp production in the Bleached Papergrade Kraft and Soda Subcategory (Subpart B) and the Papergrade Sulfite Subcategory (Subpart E) to implement BMPs to prevent or otherwise contain leaks and spills and to control intentional diversions of spent pulping liquor, soap, and turpentine. These BMPs apply to direct and indirect discharging mills within these subcategories and are intended to reduce wastewater loadings of non-chlorinated toxic compounds and hazardous substances. The same BMPs will also remove, as an incidental matter, significant loadings of color and certain oxygen-demanding substances in pulping liquors that are not readily degraded by biological treatment. EPA also expects incidental reductions in conventional water pollutants and certain air pollutants as a result of the BMPs.

EPA's legal authority to promulgate this BMP regulation is found in Section 304(e), Section 307(b) and (c), Section 308(a), Section 402(a)(1)(B), Section 402(a)(2) and Section 501(a) of the Clean Water Act, 33 U.S.C. § 1251, et seq. EPA also relies on 40 C.F.R. § 122.44(k). This BMP regulation is also consistent with the Pollution Prevention Act of 1990, 42 U.S.C. § 13101, et seq.

For authority to impose BMPs on direct discharges, EPA relies in part on section 304(e) of the Clean Water Act. EPA is authorized under section 304(e) to publish regulations on a categorical basis for certain toxic or hazardous pollutants for the purpose of controlling plant site runoff, spillage or leaks, sludge or waste disposal, and drainage from raw material storage, when the Administrator determines (1) that such incidents are associated with or ancillary to the industrial manufacturing or treatment process of point sources within the class or category, and (2) that the incidents may contribute significant amounts of toxic or hazardous pollutants to navigable waters. The BMPs in today's regulations are directed, among other things, at preventing or otherwise controlling leaks, spills and intentional diversions of phenol, acetic acid, benzoic acid, carbon disulfide, p-cresol, formaldehyde, formic acid, hydrogen sulfide, methyl mercaptan, and sodium hydroxide from spent pulping liquor at mills with pulp production in Subparts B and E. See Chapter 5. EPA has designated phenol as a toxic pollutant under CWA section 307(a)(1),

see 40 C.F.R. § 401.15, and has designated acetic acid, benzoic acid, carbon disulfide, p-cresol, formaldehyde, formic acid, hydrogen sulfide, methyl mercaptan, and sodium hydroxide as hazardous substances under CWA section 311, see 40 C.F.R. § 116.4. Turpentine, in turn, is ignitable, which is a characteristic of section 311 hazardous substances under 40 CFR Part 302. Turpentine and the wastes from which it is derived (foul condensates) also contain two listed section 311 hazardous substances--hydrogen sulfide and methyl mercaptan--and the priority pollutants phenol and toluene. Soap has a very high BOD₅ content and contains materials that exhibit significant toxicity to fish (see Section 5.6 for further discussion).

The Administrator has determined that leaks, spills and intentional diversions of spent pulping liquor containing these pollutants are associated with various chemical pulping processes discussed in Chapter 6, *infra*. The Administrator has also determined, for the reasons set forth in Chapter 5, that failure to prevent or control the leaks, spills and intentional diversions of spent pulping liquor could cause significant amounts of phenol and the identified hazardous substances to enter the Nation's waters. In addition to phenol and the § 311 hazardous pollutants identified above, EPA has also identified a number of other toxic compounds in spent pulping liquors from bleached papergrade kraft and sulfite mills that can have significant adverse effects on navigable waters. These toxic pollutants are identified in Table 5-9, *infra*. Chapter 5, *infra*, also discusses the effects of spent pulping liquor and soap on the toxicity of mill effluent. EPA intends that the BMPs established in this regulation will control the toxic effects of these pollutants. As the U.S. Court of Appeals for the D.C.Circuit observed after reviewing the goals of the Clean Water Act and its legislative history, "The indications are abundant that EPA was intended to possess broad latitude in identifying and regulating suspected toxics." NRDC v. EPA, 822 F.2d 104, 118 (D.C. Cir. 1987)(upholding EPA regulation requiring information in permit applications regarding effluent characteristics); see Statement of Sen. Muskie (Dec. 15, 1977), 95th Cong., 2d Sess., reprinted in A Legislative History of the Clean Water Act of 1977, Vol. 3, at 453-54 (1978) (citing a spill of mirex to illustrate need for § 304(e) authority, even though mirex is not designated as a § 307(a) toxic pollutant or a § 311 hazardous substance).

For authority to impose BMPs on direct discharges, EPA also relies on sections 402(a) and 501(a) of the Clean Water Act and 40 C.F.R. § 122.44(k) of EPA's regulations. Under section 402(a)(1), the Administrator is authorized to issue a permit "upon condition that [the] discharge will meet either all applicable requirements under sections 301, 302, 306, 307, 308, and 403 of this Act, or prior to the taking of necessary implementing actions relating to all such requirements, such conditions as the Administrator determines are necessary to carry out the provisions of this Act." EPA's authority to establish permit conditions under this section is very broad. See NRDC v. Costle, 568 F.2d 1369, 1380 (D.C. Cir. 1977). As applied in this context, section 402(a)(1) authorizes EPA to establish controls on "any pollutant, or combination of pollutants," for which EPA has not yet promulgated effluent limitations guidelines or standards under sections 301 or 306 that would be applicable to the permittee in question. With the exception of pH, total suspended solids (TSS) and biochemical oxygen demand (BOD), EPA has not promulgated effluent limitations guidelines or standards applicable to Subparts B and E for the pollutants associated with spent pulping liquor, soap, or turpentine. See Tables 5-1 through 5-9. While EPA expects that the BMPs will result in incidental removals of TSS and BOD, the BMPs are intended to prevent or control the releases of the other pollutants identified in the tables cited. In addition, section 402(a)(2), read in concert with section 501(a), authorizes EPA to prescribe as wide a range of permit conditions as the Agency deems appropriate in order to assure compliance with applicable effluent limits. (Section 501(a) authorizes the Administrator to carry out her functions through regulation.) EPA has determined that mills without an adequate BMP program, such as that codified in the BMP regulation, may experience undetected and uncontrolled leaks and spills that could disrupt the efficiency of their treatment systems, thus resulting in exceedances of the BAT limitations and NSPS promulgated for Subparts B and E. See, e.g., Chapter 1.

Moreover, EPA's regulations at 40 C.F.R. § 122.44(k) specifically require permit writers to impose, when applicable, BMP permit conditions to control or abate the discharge of pollutants in any case when "[n]umeric effluent limitations are infeasible" or when "[t]he practices are reasonably necessary to achieve effluent limitations and standards or to carry out the purposes and intent of [the] CWA." 40 C.F.R. § 122.44(k)(2) & (3). EPA has determined that it is

infeasible to establish numeric effluent limitations for each pollutant likely to be controlled by BMPs because leaks and spills in particular tend to be accidental, unpredictable releases and EPA is unable to specify with any degree of certainty the quantities of pollutants to be regulated. See NRDC v. Costle, 568 F.2d at 1380. Moreover, numerical effluent limitations are best suited for operational discharges deemed to represent application of best available (or demonstrated) technologies or implementation of numeric water quality criteria; they are not as effective or efficient as BMPs to prevent leaks and spills. Finally, the stated goal of the Clean Water Act is to eliminate the discharge of pollutants into the Nation's waters. CWA section 101(a)(1). EPA has determined that BMPs, by preventing or controlling leaks, spills or intentional diversions, are an important step toward that goal, particularly with respect to toxic and other pollutants. See CWA section 101(a)(1) & (3). Therefore, EPA has determined that BMPs applicable to all pollutants in a mill's spent pulping liquor, soap, and turpentine were necessary in order to carry out the purposes of the Clean Water Act and hence are authorized under section 402(a)(1) and 40 CFR 122.44(k).

Although a requirement to establish and implement BMP plans of the type described in this regulation could be imposed on a case-by-case basis under authority of section 402(a)(1) and 40 C.F.R. § 122.44(k), EPA has decided to promulgate the requirement on a categorical basis for the class of facilities subject to Subparts B and E of Part 430 under section 304(e) and under its broad authority conferred by section 501(a). Section 304(e) expressly authorizes EPA to promulgate BMPs by regulation on a categorical basis. The spent pulping liquors, soap, and turpentine covered by these BMPs contain numerous toxic pollutants and hazardous substances subject to section 304(e), and hence may be controlled by regulation. In addition, section 501(a) authorizes the Administrator to prescribe such regulations as are necessary to carry out her functions under the Act. EPA has determined that the BMP program of the type specified in § 403.03 is necessary to ensure that each pulp and paper mill with pulp production in Subparts B or E prevent or otherwise contain leaks and spills, and that they control intentional diversions, of spent pulping liquors, soap and turpentine. While the BMP regulation is intended to provide considerable flexibility to mills in designing their BMP programs, EPA has also determined that the various BMPs specified in the regulation represent the minimum elements of any effective

BMP program. By codifying them into a regulation of general applicability, EPA intends to promote expeditious implementation of a minimum BMP program and to assure uniform and fair application of the baseline requirements. EPA also believes that the regulation represents an appropriate and efficient use of its technical expertise and resources that, when exercised at the national level, will relieve state permit writers of the burden of implementing this aspect of the Clean Water Act on a case-by-case basis. Thus, in order to ensure that minimal BMPs are in place for mills in Subparts B and E and to promote efficient administration of the NPDES permit program, EPA is promulgating BMPs for Subparts B and E by regulation.

EPA also relies on Section 308(a) as authority to require mills to develop and implement a BMP Plan as prescribed in § 430.03, and to perform attendant monitoring and reporting functions. Section 308(a) authorizes EPA, among other things, to require owners or operators of point sources to establish and maintain records, make reports, install, use and maintain monitoring equipment, sample effluent, and provide such other information as the Administrator may require in order to carry out the objectives of the Act. Among other things, EPA expects that the permitting authority will be able to use the information to monitor the mills' compliance with the regulation's BMP implementation requirements. See Sections 308(a)(2) and 402(a)(2). In addition, EPA expects that information provided by mills under § 430.03 will assist EPA to evaluate the effectiveness of the BMP program it has designed.

An important aspect of the BMP program codified by EPA is the flexibility it provides to mills in deciding how to implement the various specified measures. This is consistent with the legislative history for Section 304(e), which EPA regards in this rulemaking as sensible direction for the BMPs, even when imposed under other CWA authorities. Statement of Rep. Roberts (Dec. 15, 1977), 95th Cong., 2d Sess., reprinted in A Legislative History of the Clean Water Act of 1977, Vol. 3, at 341 (1978). It is also consistent with EPA's practice of not prescribing specific technologies to achieve the performance objectives. By granting mills considerable flexibility to choose the most cost-effective strategies for preventing and otherwise controlling leaks, spills and intentional diversions of spent pulping liquors, soap, and turpentine, EPA intends to maximize the opportunity for the individual point source to consider various factors, e.g., the

facility's age, type of pulp processes, the physical configuration of the mill, and mill-specific constraints associated with recovery boilers and evaporator and treatment systems, when implementing the BMP program.

For authority to impose BMPs on indirect discharges, EPA relies on Sections 307(b) and (c) of the Clean Water Act. Pretreatment standards for new and existing sources under Section 307 are designed to prevent the discharge of pollutants that pass through POTWs or that interfere with or are otherwise incompatible with treatment processes or sludge disposal methods at POTWs. To determine whether pollutants associated with spent pulping liquors, soap, and turpentine that are indirectly discharged by mills in Subparts B and E interfere with POTW operations or pass through untreated, EPA reviewed data collected from 1988 through 1992 at a POTW that receives effluent from a bleached papergrade kraft mill. See Chapter 9.3.1. Prior to 1990-91, the mill had virtually no facilities for control and collection of spent pulping liquor leaks and spills. POTW discharge monitoring records show the fully treated effluent exhibited consistent chronic toxicity to *Daphnia* from April 1988 until June 1991. The data further show that the toxic effects of the POTW's effluent have been reduced since implementation by the mill of effective spent pulping liquor management and spill prevention control. See Chapters 5.4 and 9.3.1 and Tables 9-1, 9-2 and 9-3. These effluent toxicity effects can be related to the wood extractive components that are measurable by COD and are found in leaks and spills of spent kraft and sulfite pulping liquors that interfere with the performance of biological treatment systems and allow toxic pollutants to pass through inadequately treated. Indeed, evidence of such interference and pass through was found in data from this mill and the POTW, which showed higher mass effluent loadings for COD, TSS, and BOD before the mill implemented a BMP program. After the BMP program was implemented, mass effluent loadings of these pollutants were reduced. Data for COD, in particular, indicated that short-term interference of POTW operations previously observed at higher COD levels was being mitigated. See Chapter 9.3.1. These data led EPA to conclude that leaks and spills of spent pulping liquor interfered with POTW operations. Data from the mill also show the effect of inadequate turpentine control on POTW operations and caused pass through of pollutants. See Chapter 9.3.1. Soap can also exhibit toxic effects on aquatic life and biological treatment systems. See Chapter 5.6. EPA also considered a

case study of an incident in 1993 where a diversion of pulping liquor debilitated the mill's secondary treatment system and killed fish in the receiving water. See Chapter 8 for a more detailed discussion of this incident. Because direct discharging mills using these BMPs achieve very high removals and because POTWs cannot achieve similar removals in the absence of BMPs employed by the indirect discharger, EPA has determined that pollutants in spent pulping liquor, soap and turpentine, in the absence of controls on leaks, spills and intentional diversions, can cause disruption and interference and do pass through POTWs. For this reason, EPA is including as part of its pretreatment standards the requirement that mills implement BMPs in accordance with this regulation. EPA was unable to establish numeric PSES for the pollutants of concern because the interference occurred only sporadically in response to infrequent and unpredictable leaks and spills. However, EPA concluded that the BMP Program codified in section 430.03 will minimize the interference and pass through attributable to those pollutants and perhaps prevent it altogether.

3.0 WOOD COMPOSITION

The principal components of wood are cellulose, hemicelluloses, lignin, and extractives.

Cellulose is a linear polysaccharide consisting of *B-D*-glucopyranose units linked by (1-4)-glucosidic bonds. Cellulose molecules are bundled together in wood to form microfibrils, which in turn build up to form fibrils, and finally cellulose fibers. About 40% of most wood is cellulose that has a molecular weight of greater than 10,000. (1)

Hemicelluloses are composed of different carbohydrate units. Unlike cellulose, hemicelluloses are branched to various degrees, and their molecular masses are much lower. The content and type of hemicellulose found in softwoods differs considerably from that found in hardwoods. In softwoods, galactoglucomannans (15-20% by weight), arabinoglucuronoxylan (5-10%), and arabinogalactan (2-3%) are the most common hemicelluloses; in hardwoods, glucuronoxylan (20-30%) and glucomannan (1-5%) are the most common hemicelluloses. (1)

Lignin is essentially an aromatic polymer. It is formed in wood by an enzyme-initiated dehydrogenative polymerization of a mixture of three different 4-hydroxyarylpropenyl alcohols. The proportions of these alcohols vary with different wood species. Softwood lignin is largely a polymerization product of coniferyl alcohol. The aromatic content of softwood lignin, expressed as monomeric phenol, is about 50%. In hardwoods, lignin is formed by copolymerization of coniferyl and sinapyl alcohols. Lignin is probably chemically linked to hemicelluloses. The relative molecular mass of native lignin is considered infinite. Lignin imparts rigidity to the fiber walls and acts as a bonding agent between fibers. (1)

"Extractives" are components of the wood that can be extracted by organic solvents such as ethanol, acetone, or dichloromethane. Extractives include aliphatic extractives, which consist of fats and waxes; phenolic extractives, which consist of hydrolyzable tannins, flavonoids, lignans, stilbenes, and terpenes; and terpenoid compounds (found only in softwoods), which include mono-, sesqui-, and diterpenes; and various resin acids. The amount of extractives in wood varies greatly (1.5 to 5%), depending on the species, place of growth, and age of the tree (1). Many of the compounds classified as extractives, particularly the resin and fatty acids, which are

discharged in wastewaters from pulping operations, have been found to be toxic to aquatic life (2,3,4,5). Table 3-1 summarizes some of the extractives found in wastewaters from kraft, sulfite, and mechanical pulping operations. Although many of these compounds exhibit toxicity to aquatic life, they have not been designated specifically as "priority pollutants" under the CWA by EPA.

Table 3-1**Extractive Compounds Associated with Wood Pulping Operations**

Extractive Compound	Kraft Pulping	Sulfite Pulping	Mechanical Pulping
Resin Acids			
Abietic	•	•	•
Dehydroabietic	•	•	•
Isopimaric	•	•	•
Palustric	•	•	•
Pimaric	•	•	•
Sandaracopimaric	•	•	•
Neoabietic	•	•	•
Unsaturated Fatty Acids			
Oleic	•	•	•
Linoleic	•	•	•
Linolenic	•	•	•
Palmitoleic	•	•	•
Diterpine Alcohols			
Pimarol			•
Isopimarol			•
Abienol			•
12E-abienol			•
13-epimanool			•
Juvabiones			
Juvabione		•	•
Juvabiol		•	•
• 1'-dehydrojuvabione		•	•
• 1'-dehydrojuvabiol		•	•
Lignin Degradation Products			
Eugenol		•	
Isoeugenol		•	
3,3'-dimethoxy-4,4'-dihydroxystilbene		•	

Sources: Kringstad and Lindstrom, 1984 (1); Springer, 1986 (2); Leach and Thakore, 1974 (3).

4.0 WOOD PULPING AND CHEMICAL RECOVERY SYSTEMS

4.1 Pulping Processes

In 1992, the United States pulp and paper industry produced nearly 66 million tons of wood pulp by the following processes (6):

Process	Percent of Production	Thousands of Tons
Bleached Sulfate (Kraft)	45.0	29,703
Unbleached Sulfate	33.7	22,228
Semi-Chemical	6.2	4,101
Thermomechanical	5.4	3,584
Groundwood and Refiner	4.4	2,917
Total Sulfite	2.2	1,427
Dissolving and Special Alpha	2.1	1,383
Other	~1.0	600
Total	100.0	65,943

The distinguishing characteristics and major products associated with these pulping processes are summarized below.

4.1.1 Mechanical Pulp

4.1.1.1 Stone Groundwood Pulp

Stone groundwood pulp is produced by forcing logs against a grindstone by mechanical pressure. Nearly all of the log is converted into a low-grade pulp used primarily for newsprint and other products where permanence is not an important factor. Lignin, which binds wood fibers together, imparts color to pulp, and causes paper to yellow, is not removed in this process. Other products made from stone groundwood pulp include towels, inexpensive writing paper, and molded products such as egg cartons.

For newsprint production, groundwood pulp is usually blended with about 20% chemical pulp for added strength. Groundwood pulp is usually not bleached; if it is bleached, it is not bleached to a high degree of brightness. The frayed and broken fibers obtained from groundwood pulping are quick to absorb printing inks and thus are suitable for high-speed printing.

4.1.1.2 Refiner Mechanical Pulp

In this process, wood chips are passed through double-disc steel refiners, where the fibers are mechanically separated rather than ground on a stone. The fibers are frayed for better bonding, but they are not chopped indiscriminately as in the stone groundwood process. Consequently, refiner mechanical pulp is stronger than stone groundwood pulp and is more suitable for certain uses where strength is an important factor.

4.1.1.3 Thermomechanical Pulp

Thermomechanical pulp is produced by preheating wood chips with steam before refining (as described in Section 4.1.1.2). The heat acts to soften the lignin, which binds the wood fibers together, and promotes fiber separation. This process results in a stronger pulp than that produced by the groundwood process and minimizes the need for blending with more expensive chemical pulp in newsprint production.

4.1.2 Semi-Chemical Pulp

In this process, wood chips are processed in a relatively mild chemical solution before mechanical refining for fiber separation, usually with disc refiners. The chemical solution most often consists of a sodium sulfite/sodium carbonate liquor which acts to soften the lignin and promote fiber separation; thus, the product is often called neutral sulfite semi-chemical (NSSC) pulp. Other pulping liquors and chemical solutions may also be used to produce semi-chemical pulp. The yield of semi-chemical pulping depends on the specific process used; it ranges from 65 to 85%. Most semi-chemical pulp is not bleached and is used for corrugated board,

newsprint, and specialty boards. Bleached NSSC pulp can be used to manufacture writing and bond papers, offset papers, tissues, and towels.

4.1.3 Chemical Pulp

More than 90% of the wood pulp manufactured in the United States is produced by the kraft (sulfate) and sulfite chemical pulping processes (6). The purposes of chemical pulping are to remove lignin to facilitate fiber separation and to improve the papermaking properties of the fibers. The kraft process is the most widely used commercial process by far, accounting for more than 88% of U.S. wood pulp production in 1992 (6). Dissolving kraft and sulfite mills are operated to produce high-grade cellulose pulp for selected product applications. Soda pulping is similar to kraft pulping, except that sulfur is not intentionally added to the cooking liquor. A summary of the number of mills using various pulping processes is provided below (7):

Type of Mill	Number of Mills	Number of Mills With Bleaching
Kraft and Soda Mills		
Dissolving Grade Kraft	3	3
Papergrade Kraft	107	85
Papergrade Soda	2	2
Total	112	90
Sulfite Mills		
Dissolving Grade Sulfite	4	4
Papergrade Sulfite	11	10
Total	15	14

Kraft pulping entails treating wood chips in the range of 170• C under pressure with an alkaline pulping liquor that contains sodium hydroxide (NaOH) and sodium sulfide (Na₂S). The pulping liquor and pulping conditions promote cleavage of the various ether bonds in the lignin. The lignin degradation products dissolve in the liquor. Sodium sulfate (Na₂SO₄) and lime (CaO) are used to replenish the pulping liquor as part of the chemical and energy recovery operations associated with the process. Depending on pulping conditions, as much as 90-95% of the lignin

can be removed from wood in kraft pulping (1). The yield for kraft pulping is typically about 50%. In kraft pulping for the production of bleached pulp, more than 55% of the total weight of wood is dissolved in the pulping liquor.

Portions of the wood polysaccharides, especially those associated with the hemicelluloses, and most of the wood extractives, are dissolved in the kraft pulping liquor. If softwood is the raw material, the extractives can be recovered as by-products such as sulfate turpentine and tall oil. Turpentine contains a mixture of the lower terpenes, whereas raw tall oil (i.e., soap) consists mainly of fatty and resin acids. The content of residual extractives in unbleached (brownstock) pulp is low (1).

After separation from the pulp, the spent pulping liquor is evaporated to a high concentration and then burned in a recovery boiler to recover energy and inorganic chemicals, which are used to re-constitute fresh pulping liquor (1).

By comparison, lignin is solubilized in the sulfite process through sulfonation at elevated temperatures. The pulping liquor contains sulfur dioxide and alkaline oxides (sodium, magnesium, or calcium) (1). Ammonia is also used as a base chemical for sulfite pulping.

The lignin content of brownstock (unbleached) pulp manufactured for production of bleached pulp is characterized by two measures: (1) the Kappa Number¹, and (2) the Permanganate number or K Number. The K Number is a short test that can be performed within one hour and produces results that are about one-third lower than corresponding Kappa Numbers for softwood pulps and 30 percent lower for hardwood pulps. Kappa Numbers for conventionally pulped, kraft softwood brownstock pulps are generally in the range of 28 to 34; those for kraft brownstock hardwood pulps are in the range of 14 to 18. Kappa Numbers for unbleached sulfite pulps are lower than for kraft pulps, reflecting the lower amount of lignin present. Kappa

¹TAPPI Test Methods T236CM-85 (Kappa number) and UM251 (K number) (Reference 34).

Numbers for brownstock pulp that is not bleached may range from less than 60 to more than 100, which is a reflection of the higher yield desired for linerboard and other unbleached grades.

The distinguishing characteristics of the kraft and selected sulfite pulping processes are presented in Table 4-1 and are discussed further below.

4.2 Pulping and Chemical Recovery Systems

4.2.1 Kraft and Soda Pulping

Figures 4-1 and 4-2 provide simplified schematic diagrams of the kraft pulping and chemical recovery processes (8,9). Kraft pulping is economical because of the relatively efficient recovery of pulping chemicals and the energy from the pulping liquor. The kraft recovery system consists of the following major components:

- Collecting "weak black liquor" washed from pulp (12 to 20% liquor solids) and concentrating the liquor in multiple effect evaporators to "strong black liquor" (typically 50% liquor solids);
- Oxidizing black liquor, if required, for odor control at mills equipped with direct contact evaporation design recovery boilers;
- Further concentrating strong black liquor in concentrators to "heavy black liquor," typically greater than 65% liquor solids;
- Adding salt cake (Na_2SO_4) to make up soda losses (for mills with extensive TRS controls and sulfur recovery, most soda losses are made up with sodium hydroxide);
- Incinerating heavy black liquor in a recovery furnace, where the released energy is converted to steam and most of the inorganic chemicals are recovered in molten form as smelt. Some of the inorganic chemicals are recovered as the catch in air emission control systems on the recovery furnaces;
- Dissolving the smelt in a solution of weak wash from the causticizing circuit to form "green liquor";

- Causticizing the green liquor with lime to form "white liquor" for return to the digesters for pulping; and
- Reburning lime mud consisting of calcium carbonate (CaCO_3) in a lime kiln to form lime (CaO) for reuse in the causticizing circuit.

Cited references should be consulted for more detail regarding kraft pulping and recovery operations and the design of chemical process equipment. The processes for soda pulping and chemical recovery are essentially the same as those for kraft pulping; the main difference between these processes is that soda pulping does not involve the use of sulfur compounds to facilitate delignification. Hence, the TRS-related odor problems associated with kraft pulping do not occur. Soda pulping results in a lower yield and pulp strength than the kraft process. Soda pulping is most often used to pulp hardwoods.

4.2.2 Sulfite Pulping

Schematic diagrams for typical ammonia, calcium, sodium, and magnesium base sulfite pulping processes are presented as Figures 4-3 to 4-6, respectively (8,10). Mixtures of sulfurous acid (H_2SO_3) and bisulfite ion (HSO_3^-) are used to solubilize lignin. The lignin is removed from the cellulose as salts of liginosulfonic acid, and the lignin molecular structure remains largely intact. Sulfite pulping is performed over a wide range of pH. "Acid sulfite" denotes pulping with an excess of free sulfurous acid at pH 1 to 2, while "bisulfite" pulping is conducted under less acidic conditions in the range of pH 3 to 5 (8).

The primary differences among the sulfite pulping methods lie in the base chemical used for pulping and the extent of chemical recovery possible. Other than heat recovery from calcium base weak liquors, there are no feasible means for calcium recovery from calcium base liquors due to the formation of calcium sulfate. By-products or co-products (ligno-sulfates, yeasts)

can be derived from calcium base weak liquors through additional processing, but calcium is not returned to the process from those operations. In most ammonia base sulfite pulping, sulfur is recovered as SO_2 from burning the weak liquor, but ammonia is combusted and lost from the system (Figure 4-4).

The recovery systems for sodium base sulfite pulping are somewhat similar to kraft recovery systems in that the weak liquor is concentrated with evaporators and combusted in recovery boilers. A molten smelt is recovered and reconstituted, and sulfur is recovered as SO_2 and reused to prepare fresh cooking acid (Figure 4-5). Recovery of magnesium base liquors is accomplished in specially designed recovery furnaces where, unlike kraft recovery boilers, no smelt is produced. Rather, the combustion products are carried through the furnace and recovered as magnesium oxide in cyclonic separators. The separators are followed by gas/liquid contactors, where the remaining particulates and SO_2 are scrubbed with a magnesium hydroxide solution to regenerate the cooking liquor (Figure 4-6). A number of commercial sulfite liquor recovery systems are available. Figure 4-7 presents a summary of sulfite recovery systems currently in use (11).

4.2.3 Semi-Chemical Pulping

Figures 4-8 and 4-9 provide simplified schematic diagrams of a semi-chemical pulp mill utilizing continuous digestion and a fluidized bed system for treatment of NSSC waste liquor, respectively. Semi-chemical pulping liquors may range from sodium hydroxide alone (cold soda) to alkaline sulfite liquors to mixtures of sodium hydroxide and sodium carbonate to kraft green or white liquors. At semi-chemical mills co-located at kraft or sulfite pulp mills, pulping liquors are processed by cross-recovery with kraft or sulfite liquors. Where cross recovery is not feasible, the fluidized bed system illustrated in Figure 4-9, or a similar system, is usually used.

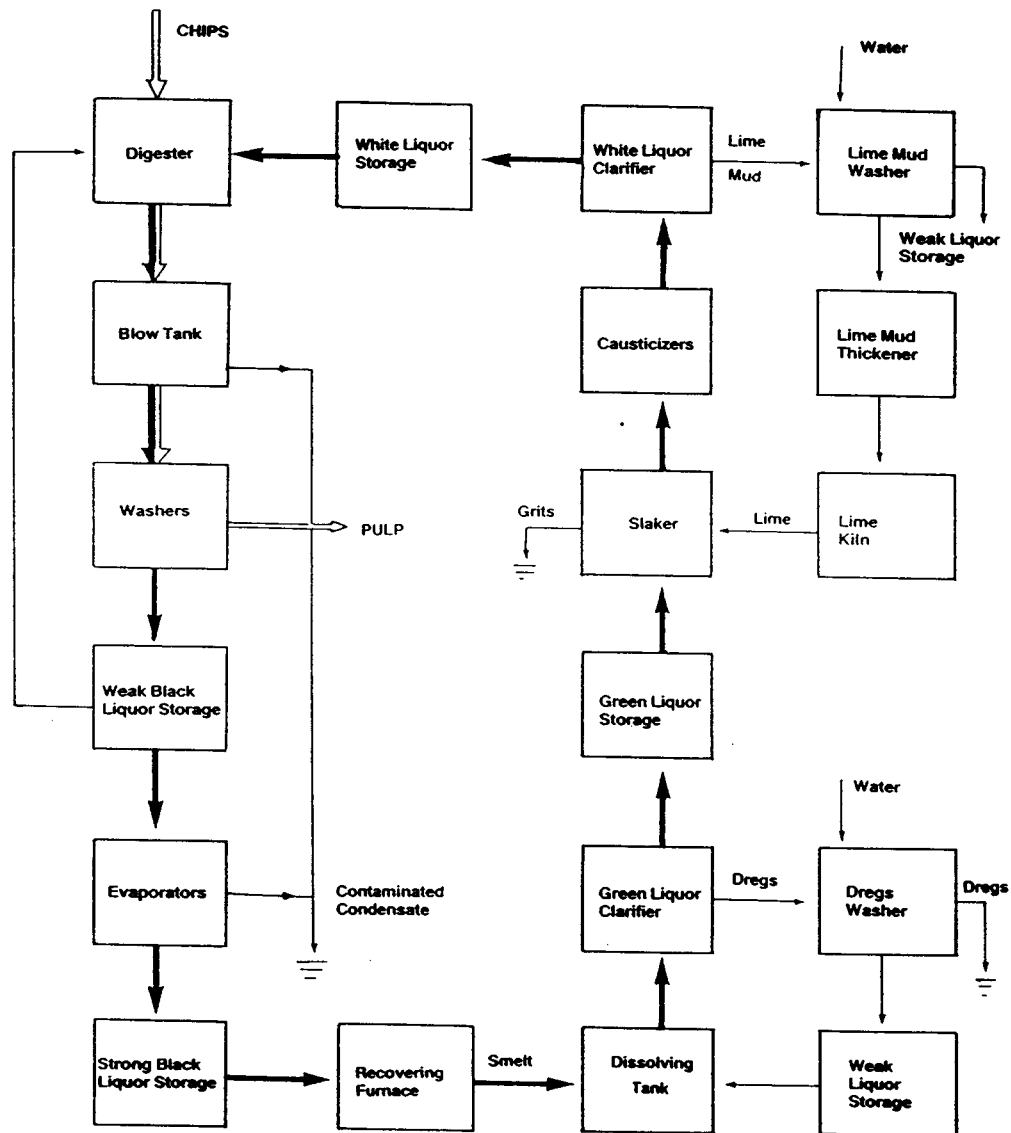
Table 4-1**Comparison of Kraft and Sulfite Pulping Processes**

Process Characteristic	Kraft Process	Sulfite Process
Cellulosic Raw Material	Almost any kind of wood, soft or hard	Any hardwood and non-resinous softwood; must be of good color and free of certain hydroxy phenolic compounds
Principal Reaction in Digester	Hydrolysis of lignins to alcohols and acids; mercaptans are formed	Sulfonation and solubilization of lignin with bisulfite; hydrolytic splitting of cellulose-lignin
Composition of Cooking Liquor	12.5 % solution NaOH, Na ₂ S, and Na ₂ CO ₃	7 % by weight SO ₂ , of which 4.5 % is present as sulfurous acid, and 2.5 % Ca, Na, NH ₃ or Mg(HSO ₃) ₂
Cooking Conditions	2 to 5 hours at 340-350 °F and 100-135 psi	6 to 12 hours at 257-320 °F and 90-110 psi
Chemical Recovery	Most of process is devoted to recovery of cooking chemicals, with energy recovery from burning organic matter dissolved in liquor. Chemical losses are replenished with salt cake, Na ₂ SO ₄ .	SO ₂ relief gas recovered; Mg or Na liquor recovered after wood digestion and washing. Ammonia can be recovered in some ammonia-base pulping systems.
Pulp Characteristics	Brown color; difficult to bleach; strong fibers; resistant to mechanical refining	Dull white color; easily bleached; fibers weaker than kraft fibers
Typical Paper Products	Strong brown bag and wrapping; multiwall bags; gumming paper; building paper; white papers from bleached kraft; paperboard for cartons, containers, and corrugated board	Book paper, bread wrap, sanitary tissue

Sources: EPA, 1982 (5); Green and Hough, 1992 (9); Ingruber, et al., 1985 (11).

Figure 4-1

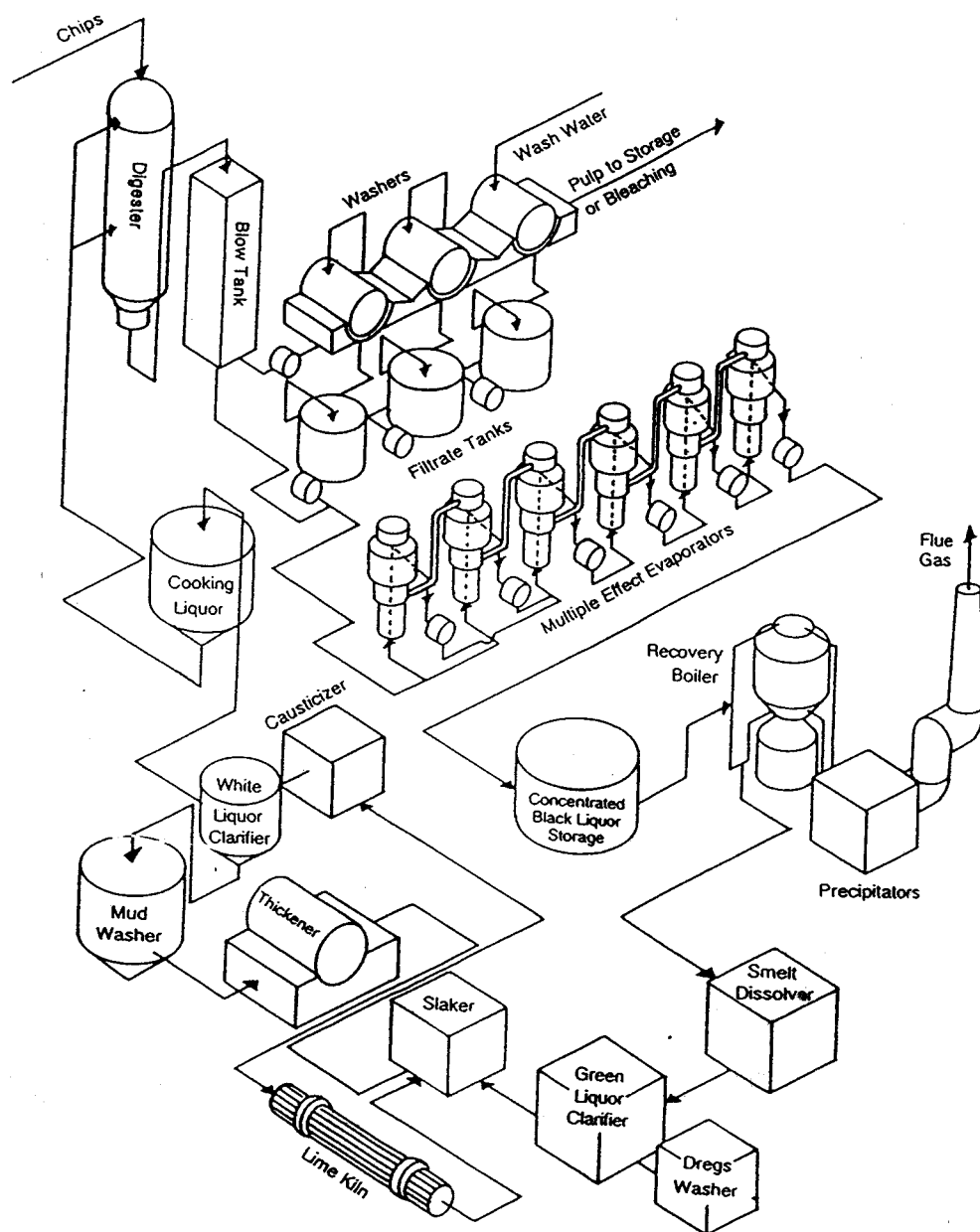
Kraft Process Simplified Schematic Diagram



Source: Smook, 1989 (8)

Figure 4-2

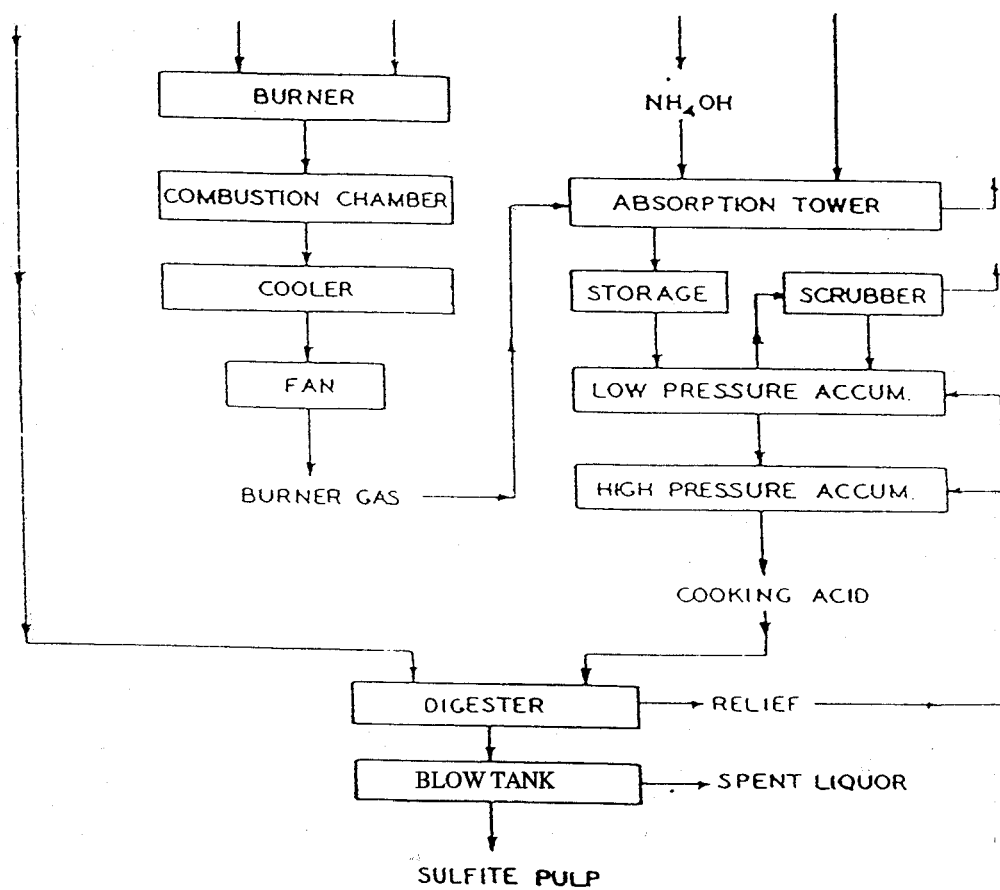
**Kraft Pulping and Chemical Recovery
Simplified Schematic Diagram**



Source: Green and Hough, 1992 (9)

Figure 4-3

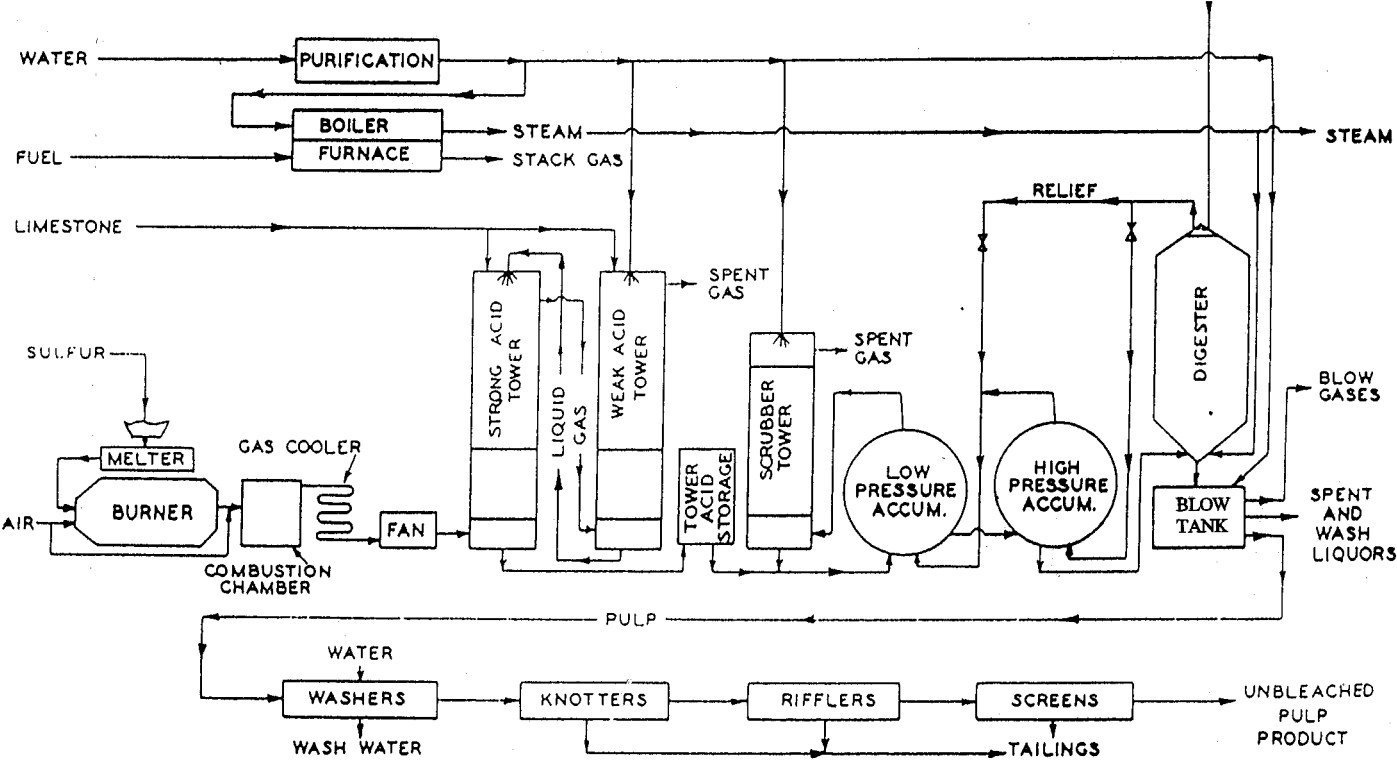
**Ammonia Base Sulfite Pulping
Simplified Schematic Diagram**



Source: Libby, 1962 (10)

Figure 4-4

Calcium Base Sulfite Pulping
Simplified Schematic Diagram

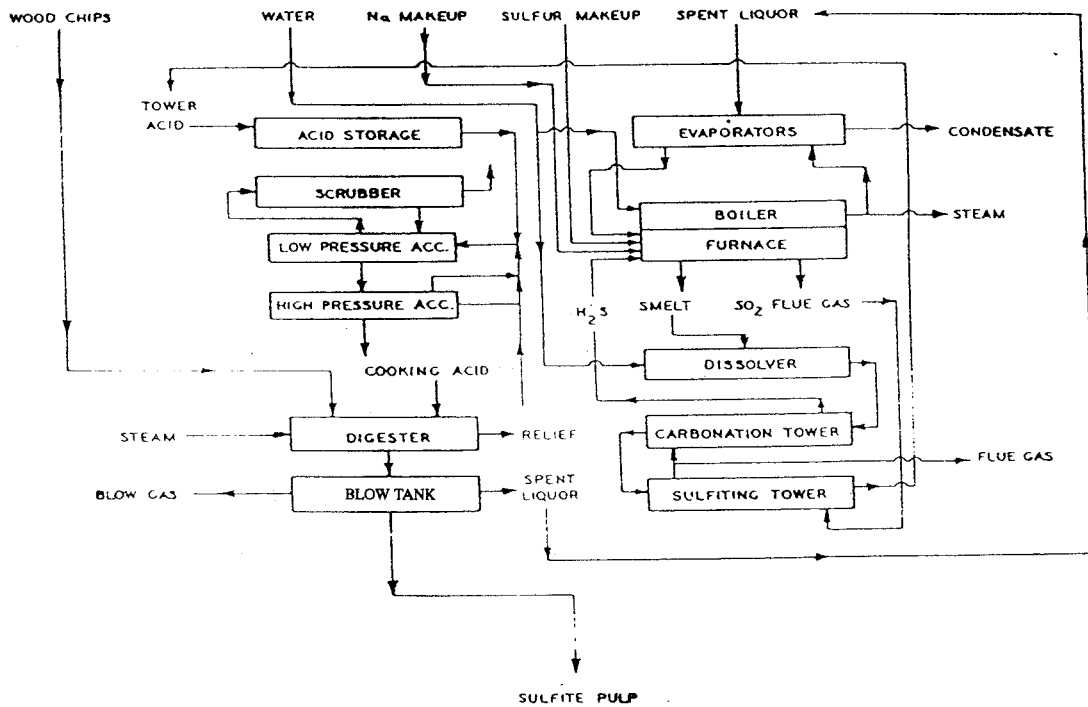


4-12

Source: Libby, 1962 (10)

Figure 4-5

Sodium Base Sulfite Pulping Simplified Schematic Diagram



Source: Libby, 1962 (10)

Figure 4-7

Sulfite Recovery Systems Currently in Use

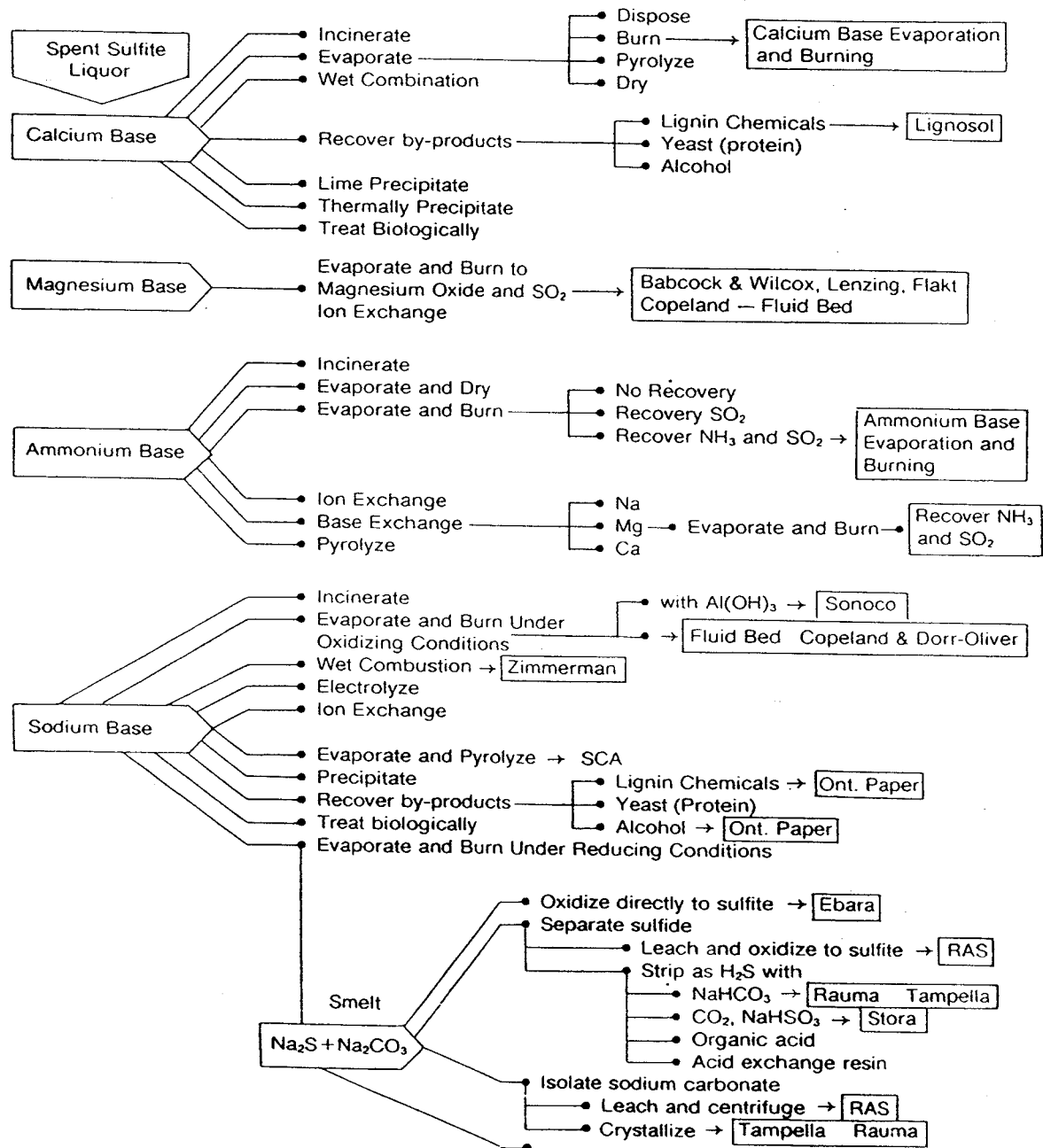
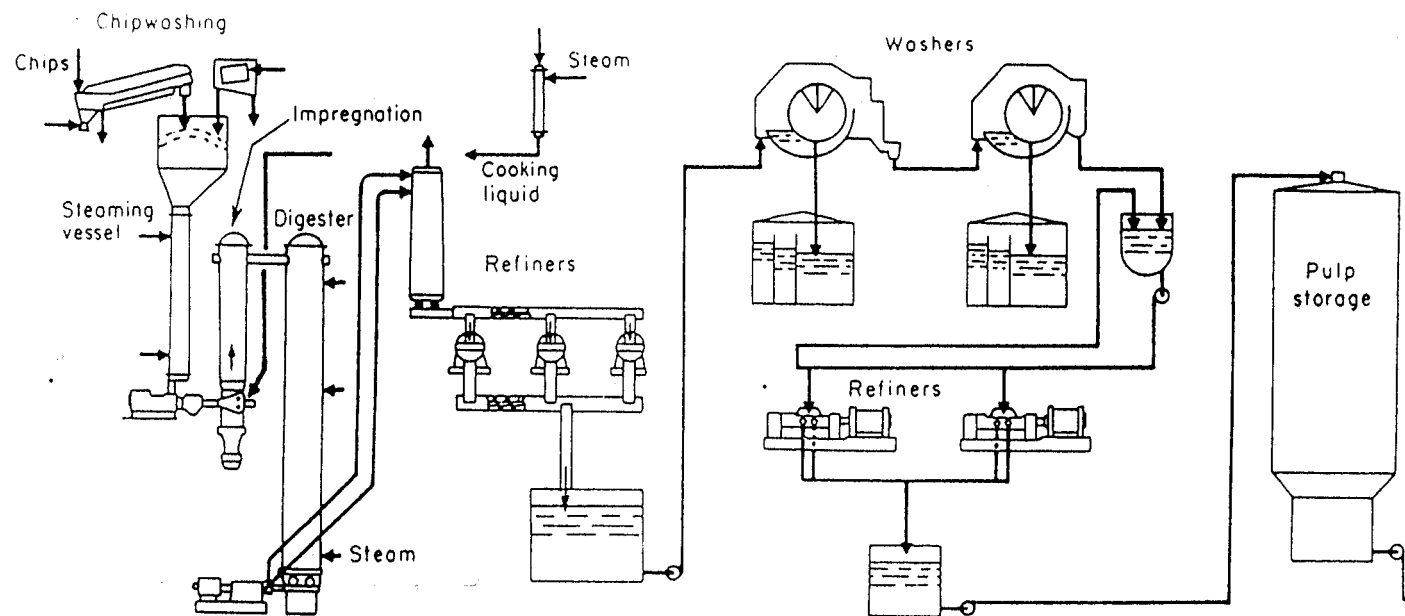


Figure 4-8

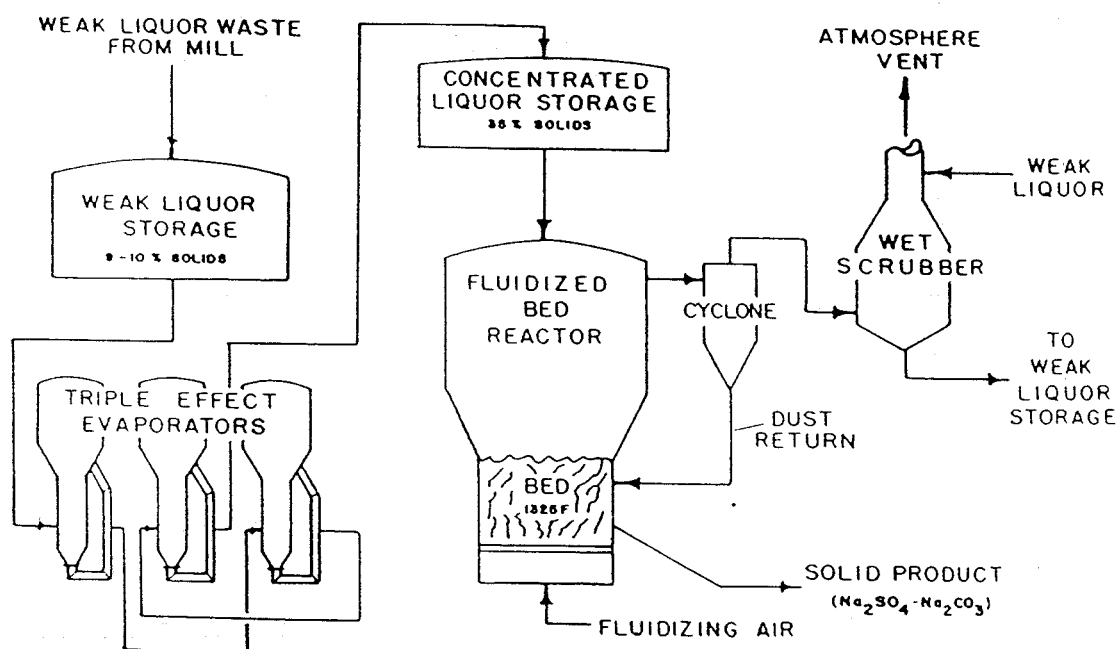
**Semi-Chemical Pulping Mill Utilizing Continuous Digestion
Simplified Schematic Diagram**



Source: Smook, 1989 (8)

Figure 4-9

**Fluidized Bed System For Treatment of NSSC Waste Liquor
Simplified Schematic Diagram**



Source: Smook, 1989 (8)

5.0 COMPOSITION AND TOXICITY OF PULPING LIQUORS, SOAP, AND TURPENTINE

5.1 Kraft Mill Black Liquor

The chemical composition of black liquor is of particular interest because of the adverse impact pulping liquors can have on biological wastewater treatment facilities, the potential for discharge of chemicals toxic to aquatic life, and the emission of TRS and HAPs to the air.

Weak black liquor recovered from brownstock pulp washing may have a liquor solids content ranging from about 12% to as high as 20%, depending on the brownstock washing systems used and the mill's operating practice. The typical elemental analysis for black liquor from a bleached kraft mill with a pulp mix of 80/20 softwood/hardwood and a higher heating value (HHV) of 6,030 British thermal units per pound (BTU/lb) of liquor solids is as follows (8):

Constituent	Percent of Black Liquor Solids
Sodium (Na)	19.2
Sulfur (S)	4.8
Carbon (C)	35.2
Hydrogen (H)	3.6
Oxygen (O)	35.2
Potassium (K)	1.0
Chloride (Cl)	0.1
Inerts	0.2

Liquors that have greater heating values (up to 6,500 BTU/lb of liquor solids) will tend to have a higher fraction of carbon, and less oxygen and sodium; the opposite is true of liquors that have lower heating values (9).

The primary inorganic constituents in black liquor include:

- Sodium Hydroxide (NaOH);
- Sodium Sulfide (Na₂S);

- Sodium Carbonate (Na_2CO_3);
- Sodium Sulfate (Na_2SO_4);
- Sodium Thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$); and
- Sodium Chloride (NaCl).

These compounds originate from the white liquor used for pulping, although small amounts may also be introduced with the wood (9). Table 5-1 presents a summary of the inorganic content of black liquors measured at 27 kraft mills (9). Dissolved wood substances in black liquors consist of four types of substances: (1) ligneous materials (polyaromatic in character); (2) saccharinic acids (degraded carbohydrates); (3) low-molecular-weight organic acids; and (4) extractives (resins and fatty acids) (9). The organic constituents are combined chemically with sodium hydroxide in the form of sodium salts. Considerable differences in liquor quality from pulpwoods are reported, particularly between softwoods and hardwoods (9). Typical ranges of black liquor solids are listed below:

Constituent	Percent of Black Liquor Solids
Alkali Lignin	30-45
Hydroxy Acids	25-35
Extractives	3-5
Acetic Acid	5
Formic Acid	3
Methanol	1
Sulfur (S)	3-5
Sodium (Na)	17-20

Table 5-2 presents supplemental detailed data for black liquor components for four pine liquors and one spruce liquor (9).

5.2 Sulfite Pulping Liquors (Red Liquors)

Table 5-3 presents the compositions of one calcium base and two magnesium base sulfite pulping liquors, and Table 5-4 presents the compositions of four ammonia base and twelve sodium base

sulfite pulping liquors (11). The ammonia base liquors have higher levels of organic materials, as measured by BOD₅, COD, and dissolved organic compounds; are about an order of magnitude more toxic than calcium base and magnesium base liquors; and are about five times more toxic than sodium base liquors. The toxicity emission factors (TEFs) presented in Tables 5-3 and 5-4 are based on static 96-hour bioassays and are factored to the volume of liquor production. The presence of ammonia compounds in ammonia base liquor is the likely cause of the higher toxicity.

5.3 Semi-Chemical Pulping Liquors

The compositions of typical NSSC fresh and spent pulping liquors are presented in Tables 5-5 and 5-6, respectively (11).

5.4 Toxicity of Pulping Liquors

The toxicity of wood pulping liquors has been extensively studied for many years. The National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI, formerly the National Council of the Pulp, Paper and Paperboard Industries for Stream Improvement) conducted studies with the Institute of Paper Chemistry in the 1940s and 1950s to determine the toxicity of components of kraft mill pulping wastes (12,13,14). NCASI reported minimum lethal concentrations of several compounds for certain species of *Daphnia* and *Pimephales promelas* (fathead minnows). These concentrations are summarized in Table 5-7.

The results presented in Table 5-7 show that hydrogen sulfide, methyl mercaptan, crude sulfate soap, and sodium salts of fatty and resins acids are among the components of black liquor that are toxic to *Daphnia* and freshwater minnows. Minimum lethal concentrations in the low parts per million (ppm) were found for these compounds. McKee and Wolf also summarized compilations of toxicity data for components of sulfate (kraft) liquors to fish (15). These data (some of which are included in Table 5-7) are presented in Table 5-8.

More recent studies of in-mill toxicity at a northern Ontario (Canada) bleached kraft mill resulted in the following recommendations to reduce effluent toxicity (in priority ranking) (16):

- Improve black liquor spill control system;
- Provide total countercurrent recycle of brownstock washers;
- Dedicate No. 1 Mill to hardwood production;
- Improve condensate system;
- Improve digester plant;
- Eliminate liquor carryover to blow heat condensate;
- Upgrade No. 1 Mill evaporators; and
- Improve soap recovery.

At this mill, the pulp mill sewer was found to contribute 55% of the effluent toxic loading, while the combined condensate and (bleach plant) acid sewer contributed 25% and 20%, respectively. Of the eight recommendations to reduce effluent toxicity, the two with the highest priority (and five of the eight recommendations), were directed at reducing the amount of black liquor lost from the processes. Improvements to the black liquor spill control system were cited as the measures that would have the greatest impact on reducing effluent toxicity.

Toxic impacts to the aquatic environment by compounds associated with kraft pulping liquors have also been reported. A large spill of black liquor from a kraft mill resulted in "massive fish mortalities" at the time of the spill. It was estimated that natural recolonization of the river by native fish would take several years (17). In another well documented case, a large release of spent pulping liquor and contaminated condensate resulted in failure of the wastewater treatment plant which, in turn, resulted in an NPDES permit exceedance and a moderate fish kill in the receiving river (32, 33). Also, sublethal toxic effects in rainbow trout have been attributed to the accumulation of dehydroabietic acid discharged from a kraft mill (18).

At a large southern United States bleached kraft paperboard mill, the process wastewater effluent is discharged to a local POTW; this wastewater comprises more than 95% of the combined industrial and municipal wastewater volume treated at the POTW. The POTW provides biological treatment with an aerated stabilization basin similar to those installed at many kraft

mills. A portion of the pulp produced at the mill is bleached. Prior to 1990-1991, the mill had essentially no facilities for the control and collection of black pulping liquor spills and leaks. POTW discharge monitoring records show the fully treated effluent exhibited consistent chronic toxicity to *Daphnia* from April 1988 until June 1991.

During 1989 and early 1990, when the mill was undergoing extensive upgrading, POTW operating records document over 100 incidents of black pulping liquor losses from the mill. During that time, there were numerous violations of the POTW NPDES permit effluent limitations for TSS, BOD₅, and toxicity effluent limitations. NPDES permit operating data for the period of December 1988 through December 1992 showed intermittent acute toxicity of the effluent to *Daphnia* from mid-1989 through early 1990, and consistent chronic toxicity to *Daphnia* until mid-1991, at which time installation of most of the spent pulping liquor spill prevention and control facilities was completed (19).

The mill underwent a major upgrade during much of 1989 and early 1990. A series of construction problems resulted in heavier-than-normal black liquor losses to the sewer, which hampered POTW operations. POTW performance with respect to conventional pollutant discharges improved in 1992, coinciding with implementation of effective spent pulping liquor management, spill prevention, and control at the mill (see Section 9.4).

5.5 Toxic Pollutants Found in Spent Pulping Liquors

EPA collected samples of spent pulping liquors from four kraft mills and one sulfite mill for analysis of toxic wastewater pollutants and volatile organic compounds, including HAPs. The results of these analyses are presented in Table 5-9. These data show that phenol was detected in sulfite red liquor at 882 • g/L, and in samples of hardwood and softwood kraft black liquor at concentrations ranging from 1,200 micrograms per liter (• g/L) to more than 50,000 • g/L, which exceeds the water quality criteria for phenol. See 45 Fed. Reg. 79318, 79338 (November 28, 1980) and supporting record. Based on this information, EPA has determined that spills, leaks or intentional diversions of spent pulping liquor could contribute significant amounts of phenol to

U.S. waters. One softwood black liquor sample was analyzed for zinc and found to contain 272 • g/L. This level, though significant, is below chronic and acute water quality standards (31). However, it has been EPA's longstanding view that the appearance of a chemical on the section 307(a) toxic pollutant list indicates the potentially toxic effects of its discharge. See 44 Fed. Reg. 32854, 32897 (June 7, 1979) (promulgation of general 304(e) BMP regulations).

In addition, the following compounds found in spent pulping liquors and/or turpentine (and the wastes from which it is derived) have been identified in EPA's list of hazardous substances as codified at 40 C.F.R. §116.4: acetic acid, benzoic acid, carbon disulfide, *p*-cresol, formaldehyde, formic acid, hydrogen sulfide, methyl mercaptan and sodium hydroxide. EPA has examined the levels of these substances present in spent pulping liquor and, in the case of hydrogen sulfide and methyl mercaptan, turpentine as they relate to potential releases that are preventable through implementation of BMPs. "Average" preventable daily releases, "maximum" releases (determined by adjusting the average daily release to account for variability in release volumes at a mill prior to implementation of BMPs), and a "catastrophic" spill (based on failure of a 300,000 gallon spent pulping liquor storage tank) were used as a basis for quantifying the potential avoided releases of hazardous substances listed. The analysis showed that potential releases of acetic acid and formic acid exceeded the "minimum reportable quantity limit", as defined in 40 CFR 302.4, for both the maximum release and catastrophic spill scenarios (35). Therefore, EPA has determined that spills, leaks, or intentional diversions of spent pulping liquors and turpentine could contribute significant amounts of hazardous substances to U. S. waters.

5.6 Toxic and Hazardous Pollutants Found in Turpentine and Soap

Turpentine and soap (tall oil), commonly called wood extractives, are normal components of kraft mill spent liquor resulting from cooking the wood in a mixture of alkaline chemicals under the normal manufacturing conditions. By weight, extractives comprise about 5% of wood, but in terms of total COD are about 8% because of the high carbon content of many of the compounds. Some components, such as methanol, are a result of chemical reactions that degrade other constituents of the wood, particularly lignin. However, the majority of the compounds come

from the resinous material in softwood, commonly called pitch. For practical purposes there are virtually no similar components in hardwoods.

Crude sulfate turpentine (generally known as simply "turpentine" in the kraft industry) is a complex mixture of volatile compounds obtained from the pitch component of wood. Turpentine leaves the kraft manufacturing process with the foul condensates formed when steam from the cooking and black liquor evaporation is condensed.

Turpentine is relatively easy to separate from the digester blow condensate, both batch and continuous, by decanting it and removing the top layer containing the insoluble turpentine. Crude turpentine is often sold to reprocessors who purify it for sale to end users. It is also frequently used as a fuel in the mill, effectively destroying all organic components, including the priority pollutants.

Table 5-10 shows the major components of kraft foul condensates and their location in the process. Two of the compounds listed as phenolics are phenol and toluene. Both compounds are on the list of priority pollutants. Many other compounds found in crude turpentine are extremely toxic and in addition, turpentine is ignitable.

There is no specific data available on the fraction of the contaminants in the foul condensates that remain with the separated turpentine, but in view of the relatively simple flotation type separation systems used, and the well known tendency for the separation to fail from time to time due to carry-over of black liquor, it is apparent that most of the contaminants found in the condensates were also found in the turpentine at least on occasion.

In addition to high BOD₅ content¹, soap and some of its constituents have been shown to be highly toxic to fish, with minimum lethal concentration levels similar to listed hazardous substances (see Tables 5-7 and 5-8). A 1947 NCASI technical bulletin (12) identified sulfides,

¹Reported to be as high as 850,000 to 950,000 mg/L at one mill (26).

5.0 Composition and Toxicity of Pulping Liquors

mercaptans, and soap components as the kraft pulping liquor constituents with greatest potential for harming aquatic life if released in abnormally large quantities.

Table 5-1

**Inorganic Content of Black Liquors
(Weight Percent, Dry Solids Basis)**

Constituent	Average	Minimum	Maximum
Sodium Carbonate	8.7	6.6	12.3
Sodium Sulfate	3.2	0.9	8.3
Active Alkali as Na ₂ O	6.0	3.9	8.6
Sodium	18.7	17.2	20.5
Potassium	1.4	0.4	2.7
Sulfur	3.8	2.6	6.2
Sulfated Ash	62.1	57.3	69.2

Source: Green and Hough, 1992 (9)

Table 5-2

**Components in Black Liquors
(Weight Percent, Dry Solids Basis)**

Component	Pine Liquor	Pine Liquor	Pine Liquor	Pine Liquor	Spruce Liquor
Lignin	28.9	30.7	31.1	42	41
Hemicellulose and Sugars	1.14	0.11	1.3		
Extractives	6.69	2.53	5.7		3
Saccharinic Acids			18.8		28
Acetic Acid*	3.52	2.08	5.2	3.83	5
Formic Acid*	4.48	2.7	3.1	3.37	3
Other Organic Acids	5.5	2.22			
Methanol					1
Unknown Organic Compounds	19.0	29.5	5.8	25.6	
Inorganic Salts	18.6	18.5	20.3	25.6	
Organically Combined Sodium	10.1	10.3	8.7		
Unknown Inorganic Compounds	2.08	1.35			
Sulfur					3
Sodium					16
Total	100	100	100	100	100

*§ 311 hazardous substance

Source: Green and Hough, 1992 (9)

Table 5-3

**Composition of Calcium Base and Magnesium Base
Sulfite Pulping Liquors**

Characteristic	Calcium Base	Magnesium Base		
	Mill 3	Mill 1	Mill 4B	Average
Pulp Yield (%)	46	54	45	50
Liquor Volume ⁽¹⁾ (m ³ /ODT)	9.28	6.56	5.61	6.08
pH	5.3	3.4	3.3	--
TOC (kg/ODT)	NT ⁽²⁾	NT ⁽²⁾	NT ⁽²⁾	NT ⁽²⁾
BOD (kg/ODT)	357	169	275	222
COD (kg/ODT)	1,533	807	1,144	975
Dissolved Organics (kg/ODT)	1,043	651	913	782
Dissolved Inorganics (kg/ODT)	250	173	79	126
UV Lignin (kg/ODT)	800	469	533	501
Total Sugars (kg/ODT)	264	94	165	129
Reduced Sugars (kg/ODT)	238	32	180	106
TEF ⁽³⁾	422	316	NT ⁽²⁾	--

- Notes:
- (1) Estimated liquor volume a few minutes before "blow."
 - (2) NT - Not Tested.
 - (3) TEF - Toxicity Emission Factor
(100%/96hr LC₅₀, %) × Liquor Volume (m³/ODT pulp)
(TEF approach in Table 5-3 was not developed by EPA.)

Source: Ingruber, et al., 1985 (11)

Table 5-4**Composition of Ammonia Base and Sodium Base Sulfite Pulping Liquors**

Characteristic	Ammonia Base (4 Mills)			Sodium Base (12 Mills)		
	Average	Minimum	Maximum	Average	Minimum	Maximum
Pulp Yield (%)	42.5	41	45	62	50	80
Liquor Vol ⁽¹⁾ (m ³ /ODT)	9.46	9.11	9.73	7.10	4.92	10.67
pH	--	1.5	3.3	--	2.1	4.8
TOC (kg/ODT) ⁽⁴⁾	NT ⁽²⁾	NT ⁽²⁾	NT ⁽²⁾	697	322	1,652
BOD (kg/ODT)	413	319	464	235	151	371
COD (kg/ODT)	1,728	1,553	1,872	938	476	1,757
Dissolved Organics (kg/ODT)	1,223	1,167	1,283	595	188	1,178
Dissolved Inorganics (kg/ODT)	12.5	7.0	20	226	95	348
UV Lignin (kg/ODT)	892	822	1,009	410	202	853
Total Sugars (kg/ODT)	288	210	329	137	52	278
Reduced Sugars (kg/ODT) ⁽⁴⁾	212	160	257	74	11	218
TEF ⁽³⁾	3,663	3,313	4,378	714	423	1,208

- Notes:
- (1) Estimated liquor volume a few minutes before "blow."
 - (2) NT - Not Tested.
 - (3) TEF - Toxicity Emission Factor
(100%/96hr LC₅₀ %) x Liquor Volume (m³/ODT pulp)
(TEF approach in Table 5-4 was not developed by EPA.)
 - (4) Results for TOC and Reduced Sugars for sodium base liquor are based on data for 8 mills and 11 mills, respectively. Results for all other parameters are based on data for 12 mills.

Source: Ingruber, et al., 1985 (11)

Table 5-5**Composition of Typical Fresh NSSC Pulping Liquors**

Chemical Compound	Concentration (grams/liter as chemical)
Sodium Sulfite	133
Sodium Hydroxide *	5.8
Sodium Sulfate	3.2
Sodium Thiosulfate	< 0.1
Sodium Sulfide	< 0.1
Total Sodium	53.0
Total Sulfur	35.1

*§ 311 hazardous substance

Source: Ingruber, et al., 1985 (11)

Table 5-6**Composition of Typical Spent NSSC Pulping Liquors**

Characteristic	Average	Minimum	Maximum
pH	--	6.5	8.5
Total Solids (%)	12	8	22
Volatile Solids (%) (percent of Total Solids)	47.9	43	52
BOD ₅ (mg/l)	25,000	16,000	50,000
Acetate (mg/l)	18,000	12,000	20,000
Wood Sugars (mg/l) (mostly pentoses)	7,000	5,000	10,000
Lignin (mg/l)	45,000	25,000	85,000
Oxygen Consumption (mg/l)			
From KMnO ₄	65,000	55,000	142,000
From Ag-catalyzed dichromate	100,000	83,000	235,000

Source: NCASI, Technical Bulletin 83

Table 5-7

**Minimum Lethal Concentrations to Daphnia and Fathead Minnows of
Components of Kraft Pulp Mill Wastewaters**

Compound	Minimum Lethal Concentration (parts per million)	
	Daphnia	Fathead Minnows
Sodium Hydroxide *	100	100
Sodium Sulfide	10	3.0
Sodium Sulfate	5,000	1,000
Methyl Mercaptan *	1.0	0.5
Sodium Sulfite	300	--
Hydrogen Sulfide *	1.0	1.0
Sodium Carbonate	300	250
Sodium Sulfate	5000	100
Crude Sulfate Soap	5.0 - 10.0	5.0
Sodium Salts of Fatty Acid Fraction of Sulfate Soap	1.0	5.0
Sodium Salts of Resin Acid Fraction of Sulfate Soap	3.0	1.0

*§ 311 hazardous substance

Source: NCASI, 1947 (12)

Table 5-8

Critical Concentrations (Minimum Lethal Doses) to Fish of Components of Sulfate (Kraft) Liquors

Component	Critical Concentration (milligrams per liter)
Sodium Hydroxide *	100.0
Sodium Sulfide	3
Methyl Mercaptan *	0.5
Hydrogen Sulfide *	1.0
Formaldehyde *	50
Crude Sulfate Soap	5.0
Unsaponified Fraction of Sulfate Soap	6.0
Sodium Salts of Saponifiable Fraction of Sulfate Soap	3.0
Sodium Salts of Fatty Acids	5.0
Sodium Salts of Resin Acids	1.0
Sodium Oleates	5.0
Sodium Linoleate	10.0
Sodium Salts of Abietic Acid	3.0
Phytosterol	3.0
Sodium Thiosulfate	5.0
Sodium Sulfate	100
Sodium Chloride	2500
Sodium Hydrogen Sulfide *	0.5
Sodium Sulfide (as Sulfide)	1.2

*§ 311 hazardous substance

Source: McKee and Wolf, 1963 (15)

Table 5-9

**Toxic Wastewater Pollutants and Hazardous Air Pollutants Found in Spent Pulp
Liquors**

Analyte	Regulatory Status	Black Liquor Samples					Red Liquor Sample
		Mill 3	Mill 5	Mill 5	Mill 6A	Mill 6B	Mill 7
		SW	HW	SW	SW	SW	SW
		• g/L	• g/L	• g/L	• g/L ^a	• g/L	• g/L
Acetone	--	ND(500)	9,190	3,880	2,500	NA	2,320
Benzoic acid	HS	5,780	4,660	14,000	ND(50)	3,480	9,000
Benzyl alcohol	--	1,370	ND(100)	885	ND(10)	ND(100)	ND(53)
Benzanthrone	--	ND(500)	ND(500)	ND(500)	75.1	ND(500)	ND(263)
Bis(2-ethylhexyl) phthalate	HAP, PP	ND(100)	ND(100)	ND(100)	ND(10)	351	ND(53)
Butyl benzyl phthalate	PP	ND(100)	ND(100)	ND(100)	ND(10)	370	ND(53)
Carbon disulfide	HAP,HS	ND(100)	149	892	19.0	NA	ND(10)
p-Cresol	HAP,HS	ND(100)	ND(100)	ND(1000)	ND(10)	ND(100)	99.9
p-Cymene	HAP	1,140	ND(100)	ND(100)	ND(10)	180	418
p-Dioxane	HAP	ND(100)	890	ND(100)	ND(10)	NA	ND(10)
Hexanoic acid	--	ND(100)	ND(100)	ND(1000)	ND(10)	ND(100)	1,630
Methanol	HAP	377,000	NA	NA	535,000	366,000 ^b	<395,000 ^b
Methyl ethyl ketone	HAP	4,030	2,410	1,250	442	<1,290 ^b	ND(50)
Phenol	HAP, PP, HS	1,990	1,230	15,000	523	6,060	882
Alpha-Terpineol	--	4,930	322	827	ND(10)	14,700	64.6
1,3,5-Trithiane	--	73,300	ND(500)	193,000	ND(50)	74,400	ND(263)
Beryllium	PP	ND (0.06) ^c	NA	NA	NA	7.80	NA
Lead	PP	ND (5.4) ^c	NA	NA	NA	B 2.40	NA
Manganese	--	76.4 ^c	NA	NA	NA	2,290	NA

Table 5-9 (Continued)

Analyte	Regulatory Status	Black Liquor Samples					Red Liquor Sample
		Mill 3	Mill 5	Mill 5	Mill 6A	Mill 6B	Mill 7
		SW	HW	SW	SW	SW	SW
		• g/L	• g/L	• g/L	• g/L ^a	• g/L	• g/L
Sodium	HS	139,000 ^c	NA	NA	NA	13,300,000	NA
Zinc	PP	14.9 ^c	NA	NA	NA	272	NA

HW - Hardwood.

SW - Softwood.

HAP - Hazardous air pollutant.

PP - §307a Priority pollutant.

HS - §311 Hazardous substance.

ND - Not detected (at reported detection limit).

NA - Not analyzed.

^aConverted from units of • g/kg to • g/L.

^bAn average of several grab samples is shown.

^cUnits are mg/kg (sample contained 6.6% solids).

Table 5-10

Major Components Found in Kraft Condensate Prior to Separation of Turpentine

	Batch Digester Vent Condensate	Batch Digester Blow Condensate	Continuous Digester Flash- Steam Condensate	Evaporator Combined Condensate	Evaporator Condenser Condensate	Stripper Feed
Hydrogen sulfide, ppm	30-270	1-230	210	1-90	1-240	5-660
Methyl mercaptan, ppm	20-5,300	40-340	70	1-30	1-410	5-720
Dimethyl sulfide, ppm	15-7,400	40-190		1-15	1-15	10-1,000
Dimethyl disulfide, ppm	5-4,100	2-210		1-50	1-50	10-150
Methanol, ppm	1,800-12,000	250-9,100	570-8,900	180-700	180-1,200	140-10,000
Ethanol, ppm	90-3,200	20-900		1-190	1-130	20-1,100
Acetone	8-420	5-95		1-15	1-16	15-500
MEK, ppm	27			1-3	2	20-25
Terpenes, ppm	0.1-5,500	720-9,200	1,950-8,800	60-1,100	450-2,500	800-13,000
Phenolics, ppm	12				3	1-82
Guaiacol, ppm				1-10		
Resin acids, ppm				25-230		

Source: Blackwell et al (36).

6.0 SOURCES OF SPENT PULPING LIQUOR LOSSES

6.1 Kraft and Soda Mills

Losses of black liquor from kraft and soda pulping and chemical recovery processes arise from "normal" process operations, including maintenance practices; planned startups and shutdowns of evaporators, concentrators, and recovery boilers; grade changes; other intentional liquor diversions; and losses from screen rooms, brownstock washers, and deckers. In the absence of adequate collection and recovery (or controlled rate of release to the wastewater treatment plant), intentional diversions can have the same adverse impacts as a spill of similar size. Unintentional losses result from fiber and liquor spills, equipment leaks, tank overfillings, and process upsets.

The main difference between kraft and soda pulping is that sulfur compounds are not added in soda pulping. Soda pulping is less efficient than kraft pulping, which results in more black liquor production per ton of pulp and correspondingly larger recovery systems at soda mills than at equivalent-sized kraft pulp mills. Because of the absence of sulfur compounds, soda mills are not characterized by strong TRS odors and thus do not have the extensive TRS control systems common to kraft mills. Otherwise, the pulping and chemical recovery systems are similar. Based on evaluations conducted at several kraft mills and at one soda mill, EPA identified the following significant sources of black liquor losses from normal process operations:

- Leaks from seals on brownstock washers;
- Leaks from seals on pumps and valves in black liquor service;
- Intentional liquor diversions during shutdowns, startups, grade changes, and equipment maintenance;
- Sewered evaporator boil-out solutions;
- Decker losses at older mills with open screen rooms; and
- Losses from knotters and screens at mills without fiber and liquor recovery systems for those sources.

Process upsets, equipment breakdowns, tank overfillings, construction activities, and operator errors were identified as the most common sources of unintentional black liquor and causticizing area sewer losses.

6.2 Sulfite Mills and Semi-Chemical Mills

Although the pulping systems at sulfite and semi-chemical mills are based on different process chemistry and different chemical recovery facilities, spent pulping liquor losses from normal process operations and unintentional losses at these mills arise from many of the same types of sources as at kraft and soda mills.

6.3 Summary of Reported Pulping Liquor Spills

Through its Emergency Response Notification System (ERNS), EPA maintains a database of reported spills of oil and other materials. The ERNS Standard Report Database was searched for the period January 1988 to March 1993 using key words relating to pulping liquors (e.g., black liquor, green liquor, white liquor, red liquor, pulping liquor) to determine the reported number of pulping liquor spills, the volume of spilled material, the affected media, and the reported causes of the spills (20). The ERNS Standard Report Database does not contain information about environmental impacts caused by spills.

The reporting of spills by the industry does not appear to be uniform. Some of the reported spills were minor in nature and were confined to the mills. On the other hand, relatively large sewer losses of black liquor observed at a number of mills over the past few years do not appear in the ERNS Standard Report Database. Hence, the information obtained from the ERNS Standard Report Database is not considered a comprehensive measure of pulping liquor losses across the industry, especially with regard to spills and losses confined to mills and directed to wastewater treatment systems. Despite these limitations, the information regarding the causes of the spills is informative and useful for planning new and upgraded pulping liquor spill, prevention, and control programs.

A summary of the pulping liquor spills is provided in Table 6-1. The 82 reported incidents included 59 black liquor spills, 12 white liquor spills, 10 green liquor spills, and 1 red liquor spill at a sulfite mill. Table 6-1 provides a breakdown of spills between those spilled to land (soil) and those spilled to water (sewer system, basins, wastewater treatment plant, or receiving waters). Those spills to water that reach receiving waters without being contained or treated are further broken out on Table 6-1.

It can be seen that the largest portion of reported small spills (<1,000 gallons) do not reach receiving waters, whereas more than half of the reported spills greater than 10,000 gallons did reach receiving waters. Approximately 40% of those spills of unknown volume were reported to have reached receiving waters. The two spills of greater than 50,000 gallons included a 96,000-gallon black liquor spill in Maine and a 90,000-gallon green liquor spill in Florida. The ERNS reports do not include information on the effect of the spills on wastewater treatment plants or the extent of pass-through (20).

The reported causes of pulping liquor spills were as follows:

- Mechanical Failure (45%);
- Human Error (20%);
- Tank Overfilling (16%);
- Deliberate (4%);
- Weather (1%);
- Power Failure (1%); and
- Unknown (13%).

Many of the mechanical problems involved malfunctioning valves, flanges, and pumps; pipeline corrosion; and a lack of preventive maintenance. In addition to tank overfillings, which resulted primarily from human error, liquor losses attributed to human error also included improper closure of valves and vehicular accidents inside and outside the pulp mills (20).

6.4 Untreated Wastewater Loadings for Kraft Mill

Of the untreated BOD₅ wastewater loading at a kraft pulp mill with open screen rooms, about one-third can be attributed to decker filtrate; one-third to one-half can be attributed to intermittent, uncontrolled losses; and the balance can be attributed to sewerage contaminated condensates (2). Much of the BOD₅ loading from decker filtrate and intermittent, uncontrolled losses is attributable to black liquor (2).

The reduction of brownstock washing losses is an important aspect of process optimization, as well as a pollution prevention technique, particularly at bleached kraft mills, because the increased formation of chlorinated organics and higher sewer loadings of AOX and BOD₅ have been attributed to poor brownstock washing. However, spent pulping liquor losses to the pulp after brownstock washing (i.e., soda losses attributable to residual liquor remaining in the brownstock pulp after washing) are not included in this BMP discussion or in 40 CFR 430.03, since improved brownstock washing is a part of the model process technology trains considered in the development of BAT, NSPS, PSES, and PSNS for bleached papergrade kraft and soda mills.

Table 6-2 provides untreated wastewater loadings from a typical bleached kraft mill (2). These data indicate that pulping and chemical recovery processes account for nearly 15 kilograms (kg) BOD₅ per air-dried metric ton (ADMT) of pulp, or nearly 38% of the total raw waste loading. For an unbleached kraft mill, the raw waste loading from pulping and chemical recovery processes would approach 60% of the total mill loading. Nearly all of the BOD₅ loading from pulping and chemical recovery operations originates in foul condensates and losses of spent pulping liquor.

NCASI estimates that the BOD₅ loading to the recovery circuit from weak black liquor is 360 kg/ADMT of pulp (21). NCASI also advises kraft mill operators to assume 2% liquor losses in estimating emissions for Superfund Amendments and Reauthorization Act (SARA) Section 313 reporting purposes (22). These estimates imply that BOD₅ raw wastewater loadings from "normal" liquor losses are slightly more than 7 kg/ADMT. The practical lower limit in BOD₅ raw wastewater loadings that can be attained from spill prevention is reported at 5 kg/ADMT,

and the estimated BOD₅ raw waste loading from a typical kraft mill is also reported at 5 kg/ADMT for pulping and chemical recovery operations (2).

6.5 Untreated Wastewater Loadings for Sulfite Mill

Table 6-3 presents approximate untreated wastewater loadings normalized to pulp production for two sulfite mills. At both mills, most of the BOD₅ wastewater loading is associated with pulping and chemical recovery operations. For the calcium-based sulfite pulp mill, the relatively high untreated BOD₅ wastewater loadings result from the external (off-site) recovery of lignin chemicals, in which wastewaters and condensates are processed at an adjacent facility and returned to the mill for treatment and discharge.

Based on data supplied in survey questionnaires, the overall BOD₅ levels in untreated wastewaters from ammonia-based mills and specialty mills are similar to those shown in Table 6-3. By virtue of the use of similar processing steps and equipment, these mills should exhibit comparable BOD₅ and TSS loadings for the pulping, recovery and washing areas.

Table 6-1

**Summary of Reported Pulping Liquor Spills
EPA Emergency Response Notification System (ERNS) Database
(January 1988 - March 1993)**

Volume Spilled (gallons)	Number of Reported Spills			
	Total	Media Affected		
		Land	Water (All Types)*	Receiving Waters
< 100	21	18	3	3
100 to < 1,000	12	7	5	5
1,000 to < 5,000	15	9	6	5
5,000 to < 10,000	--	--	--	--
10,000 to < 50,000	5	1	4	3
> 50,000	2	1	1	1
Unknown Volume	27	11	16	11
Total	82	47	35	28

Source: EPA ERNS, 1993 (20)

*Includes sewer system, WWTP, basins, and direct to receiving waters.

Table 6-2**Typical Untreated Wastewater Loadings From a Typical Bleached Kraft Mill**

Process	Flow (m³/ADMT (%))	TSS (kg/ADMT (%))	BOD₅ (kg/ADMT (%))
Wood Yard	0.7 (4.8)	3.1 (6.2)	0.8 (2.3)
Pulping	21 (14.3)	4.9 (10.0)	9.4 (26.3)
Recovery	17 (11.9)	11.1 (22.5)	4.1 (11.4)
Bleaching	48 (33.3)	4.9 (10.0)	12.7 (35.4)
Paper Manufacturing	52 (35.7)	25.3 (51.3)	8.9 (24.6)
TOTAL	138.7 (100)	49.3 (100)	35.9 (100)

Source: Springer, 1986 (2)

Table 6-3**Examples of Untreated Wastewater Loadings for Two Sulfite Mills**

Process	Flow (m³/ADMT (%))	TSS (kg/ADMT (%))	BOD₅ (kg/ADMT (%))
Mill E - Calcium			
Acid Making, Pulping, Washing, Bleaching		32.9 (57)	69.1 (38)
External Recovery		--	77.0 (42)
Wet Air Oxidation		2.5 (4)	18.5 (10)
Paper Machines		22.2 (39)	17.7 (10)
TOTAL		57.6 (100)	182.3 (100)
Mill F - Magnesium			
Pulping and Recovery, Washing, Bleach Plant	67 (47)	34.1 (41)	71.2 (80)
Paper Machines	76 (53)	48.1 (59)	18.1 (20)
TOTAL	143 (100)	82.2 (100)	89.3 (100)

Source: EPA Mill Visit Reports: Mills E and F; 1992
Pulp, Paper and Paperboard Effluent Limitations Guidelines

7.0 SPENT PULPING LIQUOR MANAGEMENT, SPILL PREVENTION, AND CONTROL: CURRENT INDUSTRY PRACTICE

7.1 Kraft and Soda Mills

Current industry practice with regard to spent pulping liquor management, spill prevention, and control was evaluated through the performance of numerous mill visits and an evaluation of the results of a NCASI BMP survey of kraft and sulfite mills (23). Site visits were conducted at more than 30 kraft mills, 5 sulfite mills, and 1 soda mill. These mills were selected for site visits based on age, size, discharge status (direct and indirect), and pulping practice (kraft mill, soda mill, ammonia base, magnesium base, and calcium base sulfite). The kraft and soda mills ranged from mills constructed in the early 1900s to relatively new greenfield mills constructed in the mid to late 1980s. The age of the sulfite mills ranged from 70 to 90 years. The NCASI BMP survey elicited responses from more than 60 mills; site visits were conducted by EPA at many of these mills.

Information obtained from the mill visits and the BMP survey was used to classify each bleached kraft and sulfite mill subject to the BMP regulation into one of three BMP implementation categories. These initial mill classifications were supplemented and verified by mill operators through the American Forest and Paper Association (AF&PA) for virtually all bleached papergrade kraft and soda and papergrade sulfite mills subject to the BMP regulation promulgated at 40 CFR 430.03, as well as for dissolving kraft and dissolving sulfite mills (24).

Based on findings from the mill visits and on information provided by several mill operators, industry efforts at kraft spent pulping liquor management, spill prevention, and control can be classified as either mostly proactive or mostly reactive. The proactive spent pulping liquor management programs are characterized by the following features:

- Management of process operations to minimize variability to the maximum extent possible;

7.0 Spent Pulping Liquor Management, Spill Prevention, and Control:
Current Industry Practice

- A high level of management commitment, and operator awareness and training (operators are required to address spent pulping liquor losses);
- Extensive preventive maintenance programs for spent pulping liquor equipment;
- Automated spill detection and spent pulping liquor recovery systems in the pulping and recovery areas that are maintained and operated by pulping and recovery personnel;
- Secondary containment and/or high-level alarms on weak and strong spent pulping liquor tanks;
- Frequent operator surveillance of spent pulping liquor equipment and tanks, and immediate repairs to this equipment;
- Sufficient capacity (250,000 gallons to > 1,000,000 gallons) for the storage of spilled materials and planned liquor diversions;
- Systems to recover fiber and spent pulping liquor from knotting and screening operations; and
- Secondary monitoring and diversion systems for all major mill sewers that serve pulping, recovery, and recausticizing areas.

In the reactive spent pulping liquor management programs, spill response is emphasized more heavily than spill prevention. Wastewater treatment plant operators most often use conductivity monitoring systems to detect problems in the major mill sewers and at the influent to the treatment plant. Typically, it is their responsibility to notify pulping and chemical recovery superintendents of any detected problems. In these instances, the pulping and chemical recovery areas of the mills generally do not have primary responsibility for spill detection.

For many of the proactive pulping liquor management programs, engineering controls and monitoring systems observed at kraft and soda mills are consistent with those recommended by NCASI in 1974 (21). NCASI Technical Bulletin No. 276 contains recommended approaches for spill containment for all aspects of pulp and paper mill operations, sewer monitoring, and management programs.

7.1.1 Management Commitment

Operators at mills with effective control systems stress the importance of management commitment, operator awareness and training, preventive maintenance, and daily management of spent pulping liquor inventories. These factors are cited as more important than the presence of collection and containment systems. The emphasis at these mills is clearly on proactive approaches to prevent spent pulping liquor losses and spills at the process areas, rather than on reactive responses to losses and spills that occur.

At mills with effective spent pulping liquor control systems, operators conduct walk-through of critical process areas at least once per shift to identify problems. The operators can initiate minor repairs, such as tightening pump packings, on the spot. More extensive repairs are addressed through work order systems, and repairs are completed quickly.

Mill operators of the most effective spent pulping liquor control systems also conduct daily trend analyses of sewer losses at critical locations to detect low-level leaks and spills at an early stage. Most operators use conductivity to measure losses; others use COD analyses of grab or daily composite samples. At one mill, operators use a one-day BOD₅ test to detect losses of spent pulping liquor and soap. The results are plotted daily, and statistical process control is used to assist the operators in identifying trends and target areas for surveillance and repair. The target sewer-loss levels are reviewed periodically and reduced over time as part of a continuous improvement program. At this mill, shift operators are provided with information to determine spent pulping liquor loss control performance, as well as tools to correct problems as they arise, within established parameters.

Most engineers agree that it is easier to install effective spill control systems during the design and construction of new mills than to retrofit such systems into old mills. However, EPA visited two of the oldest bleached kraft mills in the United States, both originally constructed in the early 1900s. Each of these mills has two pulping lines. Each mill also has dry debarking, effective

brownstock washing, closed screen rooms, spill sumps with conductivity alarms in all black liquor areas (about five sumps at each mill), and conventional secondary biological treatment systems. Both mills have spent pulping liquor spill storage tanks considerably smaller than those discussed in Section 9.0 of this report. Neither mill has any staff dedicated to spill control, but the philosophy of "do not spill" is evident in all production activities. This philosophy has been developed by formal training and continuous emphasis on avoiding spills in daily management and supervisory activities. Neither mill has any accounting of the labor cost of spill control. Although such costs are not trivial, they are certainly less than the costs for installing extensive effluent treatment systems to achieve similar effluent quality from an equivalent mill with poor spill control. One mill discharges an average of 21 kg COD/ADMT, and the other mill discharges 28 kg COD/ADMT. Color discharges average 43 kg/ADMT and 28 kg/ADMT, respectively. These data are monthly averages. Technical personnel at these mills believe that operator training and awareness is the most significant feature of their effective spill control programs.

7.1.2 Equipment Requirements

As described above, mill operators confirm that the non-hardware aspects of spent pulping liquor management and control are by far the most important aspects of minimizing liquor losses and adverse impacts on wastewater treatment systems. Nonetheless, some hardware is necessary to effectively control and manage intentional spent pulping liquor diversions and unintentional losses and spills. Effective systems are designed with the following concepts:

- Identification of discrete spill collection areas in process areas with the potential for significant liquor and fiber losses (i.e., brownstock washing lines, evaporators, digesters, recovery boilers, tank farms, etc.) and installation of strategically located liquor collection sumps in each area;
- Diversion of clean streams from potential spill areas to avoid dilution of recovered spent pulping liquors;

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- Collection of diverted or spilled liquor at the highest possible liquor solids concentration;
- Return of collected liquor and fiber to the process at appropriate locations;
- Curbing and diking to isolate critical process areas (including soap and turpentine processing areas) from the wastewater treatment facilities; and
- Conductivity monitoring at strategic locations to detect losses and spills.

Mill operators can divert floor trench drains around brownstock washers by gravity flow to collection tanks. To further avoid dilution, weak spent pulping liquor can be used for washdowns in the washer areas. Many operators collect concentrated evaporator boil-out solutions and liquor diverted from recovery boilers during maintenance for reclamation before dilution with other waters. Several mills have installed fiber reclaim tanks and fiber filters to recover fiber from losses in the digester and washer areas. As noted above, the approach taken by many mill operators is to establish discrete spill and liquor recovery areas in critical process areas (e.g., digesters, evaporators, recovery boilers, brownstock washers, knotters, and screens) and to provide liquor collection sumps for each area. These mills use flow-through conductivity-actuated liquor collection sumps to collect liquor at preset conductivity levels that reflect liquor solids concentrations that can be recovered economically.

Figure 7-1 provides a plot of black liquor solids versus (vs.) conductivity for a southern unbleached kraft mill for a range of 0 to 16% black liquor solids (25). These data show a high correlation between conductivity and the percent of liquor solids. Although these results may not be directly applicable to all kraft mills, they are presented to demonstrate the high correlation of conductivity to liquor solids, which supports the use of conductivity as a surrogate measure of pulping liquor losses for day-to-day mill operations.

There are two approaches regarding the volume of spent pulping liquor storage capacity that is needed to operate effective spill control systems. One approach holds that the volume of available capacity should be as large as possible to allow for the collection of large volumes of

spilled or diverted liquor. The other approach holds that the volume of available spill storage capacity should be as low as possible to foster minimal process variability, more effective liquor management, and preventive maintenance.

The latter approach was found at the mills that have been operating effective spent pulping liquor control systems for many years. The large-capacity approach appears to be more prevalent in mills that are currently investigating and installing spent pulping liquor containment systems. Thus, mill operators with long and successful experience in spent pulping liquor spill control favor minimal-capacity liquor spill storage tanks, while many of those working on theoretical new designs of spent pulping liquor systems favor large-capacity liquor spill storage tanks. At mills where spill storage capacity is large, there is the potential for shift operators to pass a problem to the next shift rather than to deal with it immediately. Based on an evaluation of mills with effective spent pulping liquor control systems, a moderate amount of liquor spill capacity is necessary, but the amount should be minimized to foster spill prevention, rather than spill collection and control. A summary of black liquor storage capacity data for two kraft mills and one soda mill are presented in Table 7-1. Pulping liquor storage capacity data for three sulfite mills are presented in Table 7-2.

Process area curbing and diking are also important to isolate process areas from wastewater treatment systems by diverting spilled or diverted spent pulping liquor to appropriate liquor collection sumps and diverting stormwater "run-on" from entering liquor collection sumps, to the extent practical. Process area curbing and diking for soap and turpentine processing areas help prevent adverse impacts on wastewater treatment systems from spills and losses of these materials, which can be high in toxic materials and BOD₅. Soap is a material that is high in organic content (850,000 to 950,000 mg/L of BOD₅ reported for one mill (26)) and toxic to aquatic life and micro-organisms in biological treatment systems. Soap does not contribute significantly to conductivity; thus, soap spills and losses are not detected by conductivity-based monitoring systems unless pulping liquor is also present. Turpentine is also highly toxic and also does not contribute significantly to conductivity. Consequently, it is important to minimize the

risk of accidental losses of these materials from processing areas and storage tanks through proper operation and design, and frequent visual inspections and secondary containment where feasible. EPA site visits and the NCASI BMP survey have shown that most mills provide secondary containment for turpentine storage tanks and have taken measures to prevent turpentine and soap spills from reaching wastewater treatment systems.

7.1.3 Economical Recovery of Spent Kraft Pulping Liquors

The concentration of black liquor solids at which dilute black liquors can be economically recovered depends on several factors. The benefits of recovering black liquor losses are as follows:

- Energy value;
- Cost of replacement chemicals, primarily equivalent saltcake;
- Reduction in BOD₅ load on the effluent treatment system; and
- Reduction in color and COD discharge in the treated effluent.

The energy value and cost of replacement chemicals can readily be calculated on a mill-specific basis, while the values associated with effluent reductions are more difficult to ascertain. A brief discussion of liquor solids levels that may be economical to recover at a typical bleached papergrade kraft mill (27) is presented below.

The value of recovered chemicals is significant in cases where mills purchase saltcake. However, for today's bleached papergrade kraft mills, where high chlorine dioxide substitution and effective brownstock washing are becoming the norm, there is usually an excess of saltcake. It is likely that less than half of the bleached kraft mills in the United States can assign a credit for recovered saltcake, and that very few mills will be able to do so in the future as brownstock washing and bleaching operations are upgraded.

Assuming a typical evaporator steam economy of 4.5 (kg of water evaporated per kg of steam) and a recovery boiler efficiency of 60%, the combustion of 1 kg of black liquor solids produces sufficient steam to evaporate about 18 kg of water. The recovery of 1 kg of black liquor solids will also reduce the BOD₅ load on the effluent treatment system by about 0.15 kg, which in turn will reduce operating costs by approximately 5 cents. This amount is equivalent to the cost of steam to evaporate about 6 kg of water.

Therefore, in most bleached kraft mills where excess saltcake is produced, the financial value of recovering 1 kg of black liquor solids is equivalent to evaporating about 24 kg water (18 kg + 6 kg). In this case, the break-even liquor solids concentration, the point at which evaporation costs are equal to the value of the recovered liquor, is approximately 4%. At mills where recovered liquor will offset the need to purchase saltcake, the economical liquor solids concentration for recovery can be as low as 1%.

Where a mill lacks sufficient evaporator capacity, the break-even cost will be higher because the mill will need to allow for increasing the evaporator capacity. Conversely, there could be substantial investment and operating cost savings in cases where spent pulping liquor spill recovery systems reduce or eliminate the need for treatment of the effluent color or the expansion of a biological treatment system. Any cost credits for reducing effluent color or COD will depend on the alternative costs of compliance with each mill's discharge requirements for these pollutants, if any.

Some mills collect dilute spent pulping liquors down to 1% liquor solids and less. These mills are driven by the need to control effluent color. Other mills collect liquor solids to the point where the value of the recovered fiber, chemicals, and energy exceeds the cost of evaporating dilute liquors. These mills collect spent pulping liquor at liquor solids concentrations of 2 to 5%. As described above, this determination is highly mill-specific and depends on available evaporator capacity and saltcake balance.

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Although not required by the BMP regulation, spill prevention and control for white and green liquors at kraft mills will likely be cost-effective in many cases.

7.2 Sulfite Mills

At the sulfite mills evaluated, spent pulping liquor management, spill prevention, and control programs include many of the same features described above for kraft and soda mills. One mill has a fiber and liquor recovery system at the brownstock washers. Most of the mills do not have full secondary containment for weak and strong spent pulping liquor tanks. High-level alarms on liquor tanks appear to be standard practice. All mills are equipped with pH and/or conductivity meters and alarms at strategic locations to identify spills or upsets. Some mills have diversion tanks or ponds for large spent pulping liquor diversions or spills. Protection of the wastewater treatment facilities is the main objective for these systems. One sulfite mill reported an extensive proactive spent pulping liquor spill prevention and control program that included all of the elements described above for the kraft mills (28). The following techniques can be used to substantially minimize spent pulping liquor losses from most sulfite mills (2,28):

- Spill collection systems for the digester, pulp washing, and screening areas with recovery of fiber and spent pulping liquor losses;
- High-level alarms on spent pulping liquor and stock tanks;
- Flow recorders and continuous monitors and samplers on major process area sewers;
- Collection of tank overflows from heavy to weak liquor tanks;
- Extra equipment capacity to handle spills and upset conditions; and
- An ability to return heavy liquor and compatible boil-out solutions to weak liquor tanks instead of the sewer.

7.0 Spent Pulping Liquor Management, Spill Prevention, and Control:
Current Industry Practice

Table 7-1

**Black Liquor Storage Capacity - Kraft and Soda Mills
Tank Volume (Gallons) and Typical Operating Level (%)**

Tank	Mill A 1760 ADMT/day	Mill B 770 ADMT/day	Mill C 680 ADMT/day
Weak Liquor	852,000 (25 - 84%) 852,000 (25 - 84%)	1,500,000 (75%)	686,000 (25 - 75%)
Strong Liquor	177,000 (50%)	152,000 (90%)	158,000 (60 - 70%)
Strong Waste or Spill Tank	837,000 (0%)	345,000 (0%)	1,500,000 (30 - 35%)
Fiber Salvage	57,000 (20 - 35%)		
Intermediate Liquor		345,000 (0%)	
Wastewater Diversion Basin		5,000,000	

Source: EPA Project Files: Mill Visit Reports; Mills A, B, and C; 1992
Pulp, Paper and Paperboard Effluent Limitations Guidelines

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Table 7-2

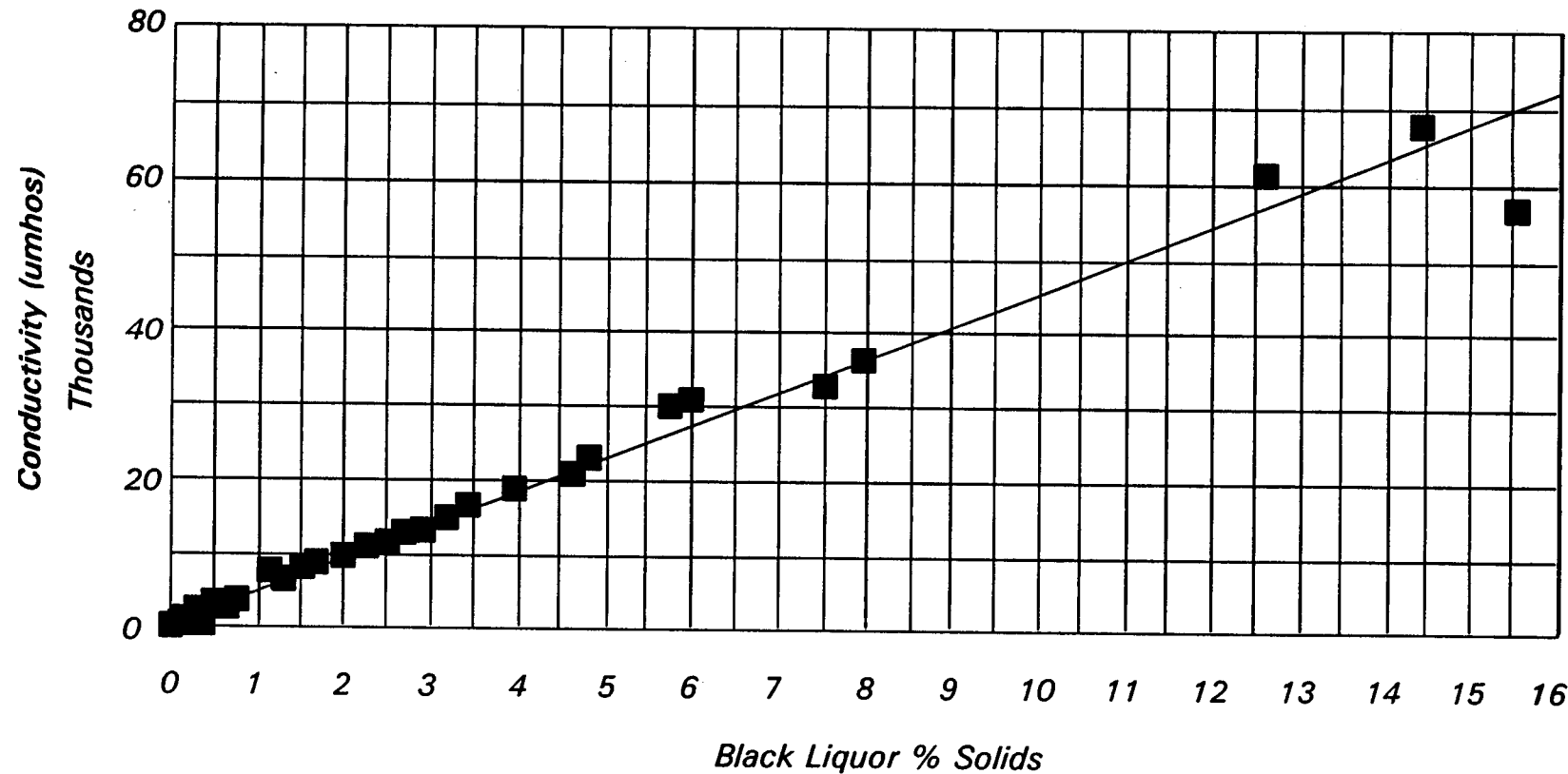
Pulping Liquor Storage Capacity - Sulfite Mills
Tank Volume (Gallons) and Typical Operating Level (%)

Tank	Mill E 180 ADMT/day	Mill F 210 ADMT/day	Mill G 140 ADMT/day
Accumulators	65,000 (80%) 95,500 (70%)	50,000 (50%)	
Fresh Acid Storage	85,000 (50%)	300,000 (65%)	
Weak Liquor Storage	88,000 (60%)	1,650,000 (50%)	
Strong Liquor Storage		1,650,000 (50%)	
Diversion Tank or Basin	1,200,000 (40%)	Not specified	5,000,000

Source: EPA Project Files: Mill Visit Reports; Mills, E, F, and G; 1992
Pulp, Paper and Paperboard Effluent Limitations Guidelines

Figure 7-1

Black Liquor Solids vs. Conductivity



R Squared = 0.976

Source: PCA, 1995 (25)

8.0 BMP REGULATORY APPROACH, REQUIREMENTS, AND IMPLEMENTATION

8.1 Regulatory Approach and Regulatory Requirements

EPA's regulatory approach for controlling losses of spent pulping liquor is to require, by regulation, that the owner or operator of each chemical pulp mill subject to the regulation implement Best Management Practices (BMPs) to prevent and control spent pulping liquor losses, other than those losses associated with normal brownstock pulp washing, and to prevent and control losses of turpentine and soap. Mills subject to the regulation are further required to prepare and maintain a BMP Plan addressing elements noted later, and to review and revise the plan as specified in the regulation. For direct dischargers, this requirement will be implemented through their NPDES permits. Existing direct dischargers are subject to the compliance dates established in the regulation, while new sources must comply immediately upon commencing discharge except where noted. As pretreatment standards, these BMP requirements apply directly to indirect dischargers, subject to the compliance dates established in the regulation.

In many respects, the BMP Plan will be similar to the Spill Prevention Countermeasure and Control (SPCC) Plans for oil spill prevention and control (see 40 CFR 112.7). The primary objective of the BMPs is to proactively prevent losses and spills of spent pulping liquors, soap, and turpentine; a secondary objective is to reactively collect, contain, recover, or otherwise control spills and losses that do occur. Pulp mill operators should ensure that no leaks or spills of spent pulping liquors are visible in their mills.

The BMPs are as follows:

1. The mill must return diverted or spilled liquor to the process to the maximum extent practicable as determined by the mill, recover such materials outside the process, or discharge spilled or diverted material at a rate that does not disrupt the receiving wastewater treatment system. Based on EPA's review of effective BMPs at selected mills, preventative maintenance practices, standard operating procedures and engineering

8.0 BMP Regulatory Approach, Requirements, and Implementation

controls are essential elements to ensure the objectives of the BMP regulation are met on a mill-by-mill basis.

2. The mill must establish a program of regular visual inspections (e.g. once per day) of process areas with equipment items in spent pulping liquor, soap, and turpentine service, and a program for repair of leaking equipment. The repair program must encompass immediate repairs when possible, and quick repair during the next maintenance outage, of leaking equipment that cannot be repaired during normal operations. The mill must also identify conditions under which production will be curtailed or halted to repair leaking equipment or to prevent spent pulping liquor, soap, and turpentine leaks and spills. Under the repair program, the mill must also establish a process for tracking repairs over time to identify equipment that may need to be upgraded or replaced, based on the frequency and severity of leaks, spills, or failures. Regular visual (and auditory) inspections by knowledgeable operators can provide an effective early warning system to detect leaks, spills and to learn about possible equipment malfunctions before they turn into more significant problems.
3. The mill must operate continuous, automatic monitoring systems that the mill determines are necessary to detect and control leaks, spills, and intentional diversions of spent pulping liquor, soap, and turpentine. These monitoring systems should be integrated with the mill process control system and may include, e.g., high level monitors and alarms on storage tanks; process area conductivity (or pH) monitors and alarms; and process area sewer, process wastewater, and wastewater treatment plant conductivity (or pH) monitors and alarms.
4. The mill must establish a program of initial and refresher training of operators, maintenance personnel, and other technical and supervisory personnel who have responsibility for operating, maintaining, or supervising the operation and maintenance of equipment items in spent pulping liquor, soap, and turpentine service. The refresher training must be conducted at least annually and should include consideration of improved BMPs as a result of experience gained in the previous year. The training must be documented, and records of training must be maintained for three years. EPA believes that initial and refresher training is necessary to ensure that operators, maintenance and supervisory personnel are familiar with the BMPs selected for implementation at the mill, and to ensure their effective implementation.
5. The mill must prepare a brief report that evaluates each spill of spent pulping liquor, soap, or turpentine that is not contained at the immediate

8.0 BMP Regulatory Approach, Requirements, and Implementation

process area and any intentional diversion of spent pulping liquor, soap, or turpentine that is not contained at the immediate process area. The report must describe the equipment items involved, the circumstances leading to the incident, the effectiveness of the corrective actions taken to contain and recover the spill or intentional diversion, and plans to develop changes to equipment and operating and maintenance practices as necessary to prevent recurrence. Discussion of the reports must be included as part of the annual refresher training.

6. The mill must establish a program to review any planned modifications to the pulping and chemical recovery facilities and any construction activities in the pulping and chemical recovery areas before these activities commence. The purpose of such review is to prevent leaks and spills of spent pulping liquor, soap, and turpentine during the planned modifications, and to ensure that construction and supervisory personnel are aware of possible liquor diversions and of the requirement to prevent leaks and spills of spent pulping liquors, soap, and turpentine during construction.
7. The mill must install and maintain secondary containment (i.e., containment constructed of materials impervious to pulping liquors) for spent pulping liquor bulk storage tanks equivalent to the volume of the largest tank plus sufficient freeboard for precipitation. An annual tank integrity testing program, if coupled with other containment or diversion structures, may be substituted for secondary containment for spent pulping liquor bulk storage tanks.
8. The mill must install and maintain secondary containment for turpentine bulk storage tanks.
9. The mill must install and maintain curbing, diking or other means of isolating soap and turpentine processing and loading areas from the wastewater treatment facilities.
10. The mill must conduct wastewater monitoring to detect leaks and spills, to track the performance and effectiveness of the BMPs, and to detect trends in spent pulping liquor losses (see section 8.2.5 below).

Mill owners or operators are required to prepare and implement a BMP Plan for spent pulping liquor, soap, and turpentine. EPA expects this plan to be proactive. The detailed provisions of

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each BMP Plan will be developed by mill operators and will be tailored to the specific circumstances at each mill. The BMP Plan should address the following general areas:

- Management Commitment and Approval;
- Employee Awareness and Training;
- Preventive Maintenance;
- Work Practices;
- Surveillance and Repair Programs;
- Engineering Analyses;
- Engineering Controls and Containment;
- Dedicated Monitoring and Alarm Systems; and
- Monitoring of BMP Implementation.

As part of the BMP Plan development, each mill must conduct detailed engineering review of the pulping and chemical recovery operations, including but not limited to, process equipment, storage tanks, pipelines and pumping systems, loading and unloading facilities, and other appurtenant pulping and chemical recovery equipment items in spent pulping liquor, soap, and turpentine service -- to determine the magnitude and routing of potential leaks, spills, and intentional diversions of spent pulping liquors, soap, and turpentine during the following periods of operation:

- Startups and shutdowns;
- Maintenance;
- Production grade changes;
- Storm or other weather events;
- Power failures; and
- Normal operations.

Maximum advantage for minimizing the potential for spent pulping liquor losses can be taken through thoughtful engineering analyses of affected process areas at each mill.

Each mill must also conduct a detailed engineering review of existing spent pulping liquor containment facilities to determine whether there is adequate capacity for the collection and

8.0 BMP Regulatory Approach, Requirements, and Implementation

storage of anticipated intentional spent pulping liquor diversions with sufficient contingency space for the collection and containment of spills, based on good engineering practice.

Secondary containment equivalent to the volume of the largest spent pulping liquor storage tank, plus sufficient freeboard for precipitation, must be provided for spent pulping liquor bulk storage tanks. Alternatively, mill operators may substitute an annual tank integrity testing program for hard secondary containment for spent pulping liquor bulk storage tanks, provided that the annual tank integrity testing program is coupled with other containment or diversion structures. Hard secondary containment must be provided for turpentine storage tanks to ensure that spills or losses of turpentine do not adversely affect wastewater treatment facilities. The flexibility to use a tank integrity testing program in lieu of secondary containment for spent pulping liquor bulk storage tanks is provided because the number of spill incidents relating to catastrophic tank failures has been relatively small, and at some mills, the location of process equipment and storage tanks would make installation of full secondary containment facilities difficult and costly in relation to the possible benefits.

The plan must include an analysis of the need for (and benefits of) continuous, automatic monitoring systems to detect and control leaks and spills of spent pulping liquor, soap, and turpentine. The monitoring plan and analysis should be conducted in conjunction with the overall engineering analysis of containment, curbing, stream segregation, operating practices, etc.

The engineering review must also consider the potential for contamination of stormwater from the immediate process areas (from digesters, evaporators, recovery boilers, etc.). Segregation and collection of contaminated stormwater from the process areas must be considered.

The plan must include a description of the monitoring program implemented to track the performance and effectiveness of the BMPs. The plan must include the statistically-derived action levels required by the BMP regulation and must also specify the period of time that the mill determines the action levels may be exceeded without triggering the responses specified in the regulation.

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The plan must include an implementation schedule not to exceed 36 months for the construction of any spent pulping liquor containment or diversion facilities necessary to fully implement the BMP Plan. An implementation schedule not to exceed 24 months should also be prepared for the installation or upgrade of continuous, automatic monitoring systems, including but not limited to, high-level monitors and alarms on existing storage tanks, process area conductivity (or pH) monitoring and alarms, and process wastewater and wastewater treatment plant conductivity (or pH) monitoring and alarms. The exact compliance dates are determined by the publication date of the regulation.

The BMP Plan must be reviewed by the senior technical manager at the mill. The BMP Plan must be approved and signed by the mill manager. A certification by a Registered Professional Engineer familiar with the facility and the requirements of the BMP regulation, although desirable, is not required by this regulation. The person signing the BMP Plan must certify to the NPDES permitting or pretreatment control authority that the BMP Plan (or amendments) has been prepared in accordance with the requirements of the regulation and in accordance with good engineering practices. Since the mill manager is ultimately responsible for approving the financial and human resources required to implement the plan, the plan must be reviewed and signed by the mill manager.

Each mill subject to the BMP regulation must amend its BMP Plan whenever there is a change in mill design, construction, operation, or maintenance that materially affects the potential for leaks or spills of spent pulping liquor, turpentine, or soap from the immediate process areas. Also, each mill subject to the regulation must complete a review and evaluation of the BMP Plan five years after the first BMP Plan is prepared and, except when amendment is required earlier due to mill changes, once every five years thereafter. As a result of this review and evaluation, the mill must amend the BMP Plan within three months of the review if the mill determines that any new or modified management practices and engineered controls are necessary to reduce significantly the likelihood of spent pulping liquor, soap, and turpentine leaks, spills, or intentional diversions

8.0 BMP Regulatory Approach, Requirements, and Implementation

from the immediate process areas, including a schedule for implementation of such practices and controls.

Except as noted below for new sources, indirect discharging mills subject to this section must meet the deadlines below. Also, except for new sources, NPDES permits must require direct discharging mills subject to this section to meet the deadlines below. If a deadline has passed at the time the NPDES permit containing the BMP requirement is issued, the NPDES permit must require immediate compliance with BMP requirement(s).

Upon commencing discharge, new sources subject to the regulation must implement all of the BMPs specified in the regulation, prepare the BMP Plan, and certify to the permitting or pretreatment authority that the BMP Plan has been prepared in accordance with the regulation, except that the action levels must be established not later than 12 months after commencement of discharge, based on six months of monitoring data obtained prior to that date.

The milestones and compliance dates for the BMP regulation are as follows:

	<u>Milestone</u>	<u>Compliance Date</u>
1.	Prepare BMP Plans and certify to the permitting or pretreatment control authority that the BMP Plan has been prepared in accordance with 40 CFR 430.03, not later than	12 months after date of publication ¹
2.	Implement all BMPs specified in 40 CFR 430.03 (c) that do not require the construction of containment or diversion instructions or the installation of monitoring and alarm systems not later than	12 months after date of publication
3.	Establish initial action levels required by 40 CFR 430.03 (h) not later than	12 months after date of publication

¹ This is the date the regulation is published in the Federal Register.

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	<u>Milestone</u>	<u>Compliance Date</u>
4.	Commence operation of any new or upgraded continuous, automatic monitoring systems that the mill determines to be necessary under 40 CFR 430.03(c)(3) (other than those associated with construction of containment or diversion structures), not later than	24 months after date of publication
5.	Complete construction and commence operation of any spent pulping liquor, collection, containment, diversion, or other facilities, including any associated continuous monitoring systems, necessary to fully implement BMPs specified in 40 CFR 430.03(c), not later than	36 months after date of publication
6.	Establish revised action levels required by 40 CFR 430.03(h) as soon as possible after fully implementing BMPs specified in 40 CFR 430.03(c), but not later than	45 months after date of publication

The time frames stated above were revised from compliance dates contained in the original proposal. These new milestone dates were developed based upon comments received by EPA and further consideration of the activities that must be completed for each milestone. The completion of the BMP Plan involves a number of complex engineering analyses that will require detailed examination of drawings, operating procedures, and maintenance records. The development of construction and monitoring approaches and schedules, required for the plan, will involve both engineering and operating personnel examining "incident scenarios" and alternative approaches. Supported by comments, EPA has determined that the BMP Plan and certain BMP elements related to the existing systems can be completed in 12 months (milestones 1, 2, and 3). Upon completion of the plan, an additional 12 months is allowed for specification of monitoring equipment, procurement, delivery, and installation (milestone 4). From the completion of the plan, 24 months are provided for those elements of the BMP implementation that require construction (sumps, tanks, valves, piping, curbs, etc.). This time span is provided to accommodate detailed engineering, design, specification, procurement, scheduling of equipment shutdowns, construction mobilization and construction (milestone 5).

8.2 Implementation Guidance for Permit Writers and Pretreatment Authorities

As described above, mill owners or operators will be required to develop and implement BMPs using practices and procedures that are tailored to the specific circumstances at each mill. To assist in the implementation of the regulation through the NPDES permit and pretreatment programs, implementation guidance for permit writers, pretreatment authorities, and the industry is provided in Sections 8.2.1 through 8.2.5.

8.2.1 Applicability of BMP Regulation to Pulping Liquors Other Than Spent Pulping Liquor

Although the BMP regulation is specific to spent pulping liquors, soap and turpentine, EPA anticipates that similar BMPs and controls may be implemented for white liquor, green liquor, and fresh sulfite pulping liquor at many mills; however, mill owners or operators are obligated to address only spent pulping liquor, soap and turpentine as part of the BMP regulation codified at 40 CFR 430.03. The regulation does not mandate that any particular types of controls be installed, nor that spent pulping liquor be recovered at any particular liquor solids concentration. Permitting and pretreatment authorities have additional authority under Section 402 of the CWA and the NPDES permit and pretreatment regulations at 40 CFR §403.5 and 122.44(k) to extend BMP requirements to other pulping liquors and other substances at pulp and paper mills, where they deem appropriate.

8.2.2 Requirements for Specific BMP Equipment Items

Secondary containment for turpentine storage tanks, and curbing or diking or equivalent containment for soap and turpentine processing areas, are required by the BMP regulation. Otherwise, the BMP regulation does not mandate that specific equipment items, monitoring systems, or alarm systems be used to comply with the regulation. EPA intends that mill owners or operators should have maximum flexibility to address management and control of spent

pulping liquor at their mills, within the context of general regulatory requirements. The specific types of equipment described in Section 9.0 were selected by EPA for the purpose of developing estimated industry-wide costs to comply with the regulation. Although these equipment items and associated control strategies are among those judged to be appropriate and effective, mill owners or operators are not constrained by the regulation to use any particular equipment item or control strategy, except that spent pulping liquor bulk storage tanks require secondary containment or annual integrity testing.

8.2.3 Costs of BMP Compliance

As part of its effort to characterize the economic impact of the effluent limitations guidelines and standards on the pulp and paper mills, EPA estimated industry-wide costs to comply with the BMP regulation (see Section 9.0). EPA believes the cost estimates presented in Section 9.0 are reasonable based on comparisons made with actual costs incurred by mill operators who have implemented effective BMP programs and based on review of independent cost estimates provided by several mill operators. The BMP regulation does not require that mill owners or operators incur a specific cost to comply with the regulation.

8.2.4 Recovery of Liquor Solids Under BMP Regulation

As described in Section 7.0, the level of liquor solids that may be economical to recover is mill-specific and depends on factors such as saltcake balance, available evaporator capacity, and the need to control effluent color and other pollutants. The BMP regulation does not mandate that mill owners or operators recover dilute liquors at a particular liquor solids concentration (e.g., 1% black liquor solids). The intent of the regulation is that mill owners or operators will determine an appropriate target level of liquor solids recovery as part of the engineering review that is required by the regulation. As mills are modernized and upgraded, EPA anticipates that new pulping and chemical recovery facilities, including additional evaporator capacity, will be designed and installed to achieve more effective spent pulping liquor control.

8.2.5 Monitoring of BMP Implementation

EPA is requiring monitoring of the BMP implementation at pulp and paper mills for two reasons: (1) to provide a framework for monitoring the performance and effectiveness of BMPs on a continuing basis; and (2) to establish an early warning system to detect trends in spent pulping liquor losses that might not otherwise be obvious. The BMP monitoring program involves establishing action levels as a measure of organic loading at the point influent enters the wastewater treatment system or at another key location or locations in the mill sewer system representative of the pollutant loading of spent pulping liquor, soap, and turpentine to the wastewater treatment system. It also involves responding to exceedances of these action levels with investigative and corrective actions, as appropriate. The BMP regulation requires mill owners or operators to establish initial action levels based on at least six months of monitoring data, and to revise these levels after the BMP Plan has been fully implemented. Exceedances of the action levels will not constitute violations of NPDES permits or pretreatment standards; however, failure to conduct the required BMP monitoring, or failure to conduct investigative or corrective actions when the action levels are exceeded (as described in the regulation), would constitute permit or pretreatment standard violations.

EPA believes that COD is among the best, if not the best, pulp mill wastewater characteristic that can be monitored to fulfill this provision of the BMP regulation. COD can measure those pollutants characteristic of spent pulping liquors that are somewhat toxic and refractory to biological treatment. The test method for COD is highly reproducible and can be performed in a short period of time, unlike the BOD₅ test method. It also has the advantage of being responsive to losses of turpentine and soap, unlike conductivity, which is not responsive to these materials. Alternative pulp mill wastewater monitoring characteristics could include Total Organic Carbon (TOC), a simplified one-day BOD₅ test, or another similar short-term measure of organic loading. The objective is to use an analytical method that can be performed within one day of sampling, which will allow for timely data assessment. The regulation provides flexibility for mill owners or operators to select any reasonable measure of organic loading and/or spent

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pulping liquor losses. The BMP regulation requires daily monitoring of the wastewater treatment system influent or, alternatively, daily monitoring at other locations selected to isolate possible sources of spent pulping liquor, soap, or turpentine from the other possible sources of organic-containing wastewaters that are tributary to the wastewater treatment system. At each location, EPA expects that mass loadings of COD, TOC, or another short-term measure of organic loading will serve as a primary indicator of how well the mills are implementing their BMP Plans.

Mill owners or operators must establish statistically-derived upper and lower action levels based on six months of monitoring data. EPA expects that these data will reflect normal mill operations, with no data reflecting abnormal spills or losses of spent pulping liquor, soap or turpentine. For example, running seven-day average 75th- and 90th-percentile values may be derived and used as upper and lower control levels. When the lower action level is exceeded, mill operators must initiate appropriate investigative actions to determine the cause of such occurrence (e.g., potential abnormal liquor losses). EPA anticipates that most mills also would initiate corrective actions at this point if appropriate. If the upper action level is exceeded for the period of time specified in the BMP Plan, mill operators must initiate corrective actions to bring the monitored mass loadings of COD, TOC, or another organic measure to a level below the lower action level as soon as practicable. Subject to reissuance dates of NPDES permits (for direct dischargers), existing dischargers must establish an initial set of action levels within 12 months from date of publication of the regulation and a revised set of action levels after the BMPs have been fully implemented, but not later than 45 months from the date the regulation is published. New dischargers must establish action levels not later than 12 months after commencement of discharge.

The approach taken here is consistent with industry practice for the monitoring of many process variables and process or equipment conditions. Process annunciator panels typically supply an alert to operators, warning that they should examine a “developing” situation, such as a tank filled to an abnormally high, though not critical, level or pressure at a pump discharge lower than normal. That same annunciator would provide an alarm, usually in the form of sound and a

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flashing light, when action is needed immediately, e.g., when damage or an irretrievable process upset is imminent. The same philosophy which has led to this process control approach can reasonably be applied to the monitoring of spent pulping liquor since some losses, such as leaks at pump seals, will develop gradually and can be investigated and repaired in response to a lower action level, while a major pipe joint failure should be dealt with by immediate action if the loss rate threatens the downstream treatment capacity, as indicated by the higher action level.

It may become necessary for the mill to establish interim action levels due to changes in mill systems and operations not associated with the implementation of BMPs. These interim action levels are a temporary measure to respond to significant changes in mill design, operation, production, or maintenance that result in the existing action levels becoming obsolete (ineffective in prompting timely investigation or action) prior to the establishment of the revised (post-implementation) action levels. Examples might be the startup of a new fiber line, long-term shutdown of a fiber line, or replacement/upgrade of a major equipment component that impacts the wastewater discharge rate significantly.

Perhaps the clearest illustration of both the potential effectiveness of BMPs and the need for initial and revised action levels is found in the actual experience of a mill that carried out a BMP program involving many of the elements required in the BMP regulation. This mill, located in the southeastern U.S., implemented a spent pulping liquor spill prevention program in 1990 and 1991. Figure 8-1 presents the 7-day running average COD data for a year prior to the implementation of the spill prevention measures (1988) and the first year after implementation (1992). The figure also includes example action levels shown at the 75th and 90th percentile levels of COD for each year. These data provide evidence of the effectiveness of BMPs in several ways (19).

First, it is clear that the baseline COD has been substantially reduced, as illustrated by the fact that the darker line (1992 data) is, at almost all times, lower than the 1988 data plot. This is also

evident from the lower COD values represented by the 1992 example action levels as compared to the 1988 action levels shown on the figure.

A second result of the implementation of the spill prevention program is the reduction in the magnitude of the of the COD excursions as illustrated by the heights of the peaks in the data which for the most part correspond to major spent pulping liquor spills or intentional diversions. The major spike in the 1992 data, occurring in June, was a result of a major turpentine spill. Had the turpentine tanks and handling equipment been included in the spill prevention program, as required by the new BMP regulation, this release may not have occurred and the overall improvement illustrated by the comparison of the 1992 and 1988 data would have been even larger. This turpentine spill and its strong detrimental impact upon the operation of the POTW is discussed later in Section 9.3.1 (19).

A review of an incident that occurred at kraft pulping mill in the Southeastern U.S. in July of 1993 provides further evidence of both the efficacy and cost-effectiveness of the implementation of BMPs as called for in 40 CFR 430.03. This mill experienced a process upset that resulted in a significant amount of foul condensate and spent pulping liquor being sewerred. When the color of the waste water treatment plant influent raised suspicions of abnormally high chemical loadings, a number of “defensive measures” were taken by the WWTP operators to maintain the health of the treatment process. Nonetheless, within two days, the treatment plant outfall exhibited depleted oxygen levels and, shortly thereafter, suspended solids in the effluent exceeded permit levels. Efforts to augment the plant bacteria inventory did not reverse the trends and a fish kill resulted downstream of the plant outfall. State officials ordered a shutdown of the mill while measures were taken to clean up and restore the WWTP to effective and consistent operation.

Actions taken after the incident provide additional evidence that BMPs are effective in reducing the level of pollutants in the mill effluent and in reducing the potential for major incidents that can render the associated waster water treatment plant ineffective. First, a detailed analysis of the

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incident showed that the absence of a feedback signal that would have provided the operators with indication of a valve position (open/closed status) allowed the upset condition to progress unchecked for some time. Had the failure of the valve to open in response to a operator command been evident from a feedback indicator signal, the upset could have been controlled early and the contaminated condensate could have been retained and returned to the process, rather than sewerred. This type of analysis is illustrative of the incident review element of the BMP plan and should virtually eliminate a repeat of the specific type of incident involved here. Additionally, the type of engineering analysis required to develop a BMP plan for this particular mill may have uncovered the potential for problems associated with the absence of a valve position indicator in the control room for this and other key valves and may have proactively avoided the upset, rather than the retrospective approach noted above.

A second message from this particular case/incident is contained in the findings of a study of the incident commissioned by the mill as part of the Consent Order that resulted from the NPDES permit violation. This study was carried out by an engineering firm during the six months immediately following the incident. The contractor examined the rate of BOD losses associated with spills (by subtraction of “baseline” BOD levels in the effluent) before and after the incident and found a 57% reduction in these losses. After examining the changes in the mill as a result of the incident, the contractor attributed the improved performance to:

- Review of the incident with operating personnel;
- Adjustments to brownstock washer operation;
- Operational and design changes in the evaporator area;
- Improved in-mill communications; and
- Supplemental training for pulp mill and evaporator personnel.

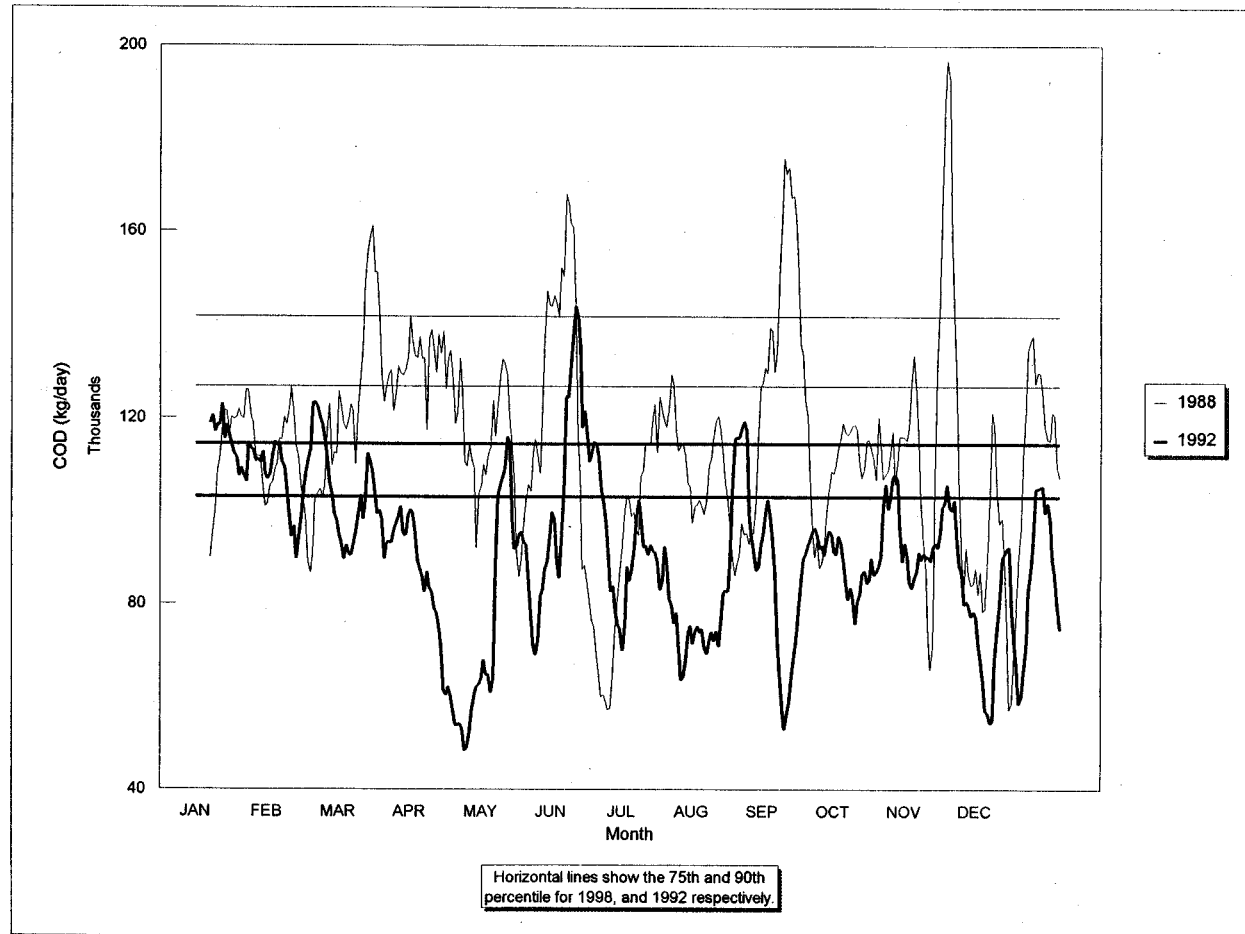
It is important of note that the mill estimated the financial cost of the incident and resulting NPDES permit exceedance to total \$2,997,730, mostly attributable to a 7.5 day mill shutdown to restore the waste water treatment plant to effective operation. The company was also required to spend an additional \$500,000 on plant improvement measures aimed at pollution prevention. In

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summary, the financial consequences of this single incident were approximately equal to the full implementation cost of BMPs as required by 40 CFR 430.03 (32, 33).

Figure 8-1

Wastewater Treatment Influent COD Levels With and Without BMPs



Source: EPA, 1993 (19)

9.0 ESTIMATED COSTS AND EFFLUENT REDUCTION BENEFITS

This section presents a discussion of the methods that were used to estimate industry-wide costs to fully implement BMPs for spent pulping liquor, soap, and turpentine at pulp and paper mills.

9.1 Current Status of Spent Pulping Liquor Spill Prevention and Control Systems in United States

A wide variety of spent pulping liquor spill prevention and control practices exist in the pulp and paper mills in the United States. Many older and complex mills have been operating proactive, highly effective spent pulping liquor spill prevention and control systems for many years. Many other mills have fairly limited spill prevention and control systems. EPA evaluated the current status of the industry using information obtained during mill visits, the results of the NCASI BMP survey, and follow-up contact with the AF&PA (24). The mills were divided into three categories, based on the status of their spent pulping liquor spill prevention and control systems, as follows:

- Category 1: Mills with most of the major components of a model spent pulping liquor control system in place. Incremental investment costs at these mills are not expected to exceed 10% of the estimated total investment costs (excluding costs for preparation of initial BMP Plan) (see Section 9.2).
- Category 2: Mills with some of the major equipment items of a model spent pulping liquor control system in place (e.g., a few liquor collection sumps, liquor storage tanks, sewer conductivity monitoring, etc.). At these mills, as much as 60% of the estimated total investment costs may be necessary to fully implement a BMP Plan.
- Category 3: Mills with relatively little spent pulping liquor control equipment in place. At these mills, as much as 90% of the estimated total investment costs may be required to implement a BMP Plan.

Table 9-1 presents the status of spent pulping liquor BMP implementation at pulp and paper mills. A summary of this status is presented below:

Type of Mill	Percent of Mills in Category 1	Percent of Mills in Category 2	Percent of Mills in Category 3
Kraft and Soda Mills	26%	29%	45%
Sulfite Mills	20%	33%	47%

9.2 Equipment Costs for BMP Implementation at Pulp and Paper Mills

To develop the industry-wide costs, bleached papergrade kraft and soda and papergrade sulfite mills were first classified by the level of complexity of their pulping and chemical recovery systems. *Single line* mills were defined as mills with one fiberline (e.g., one continuous digester or one set of batch digesters, one or two pulp washing lines, etc.). *Moderately complex* mills were defined as mills with two fiberlines. *Complex* mills were defined as mills with more than two fiberlines, multiple sets of evaporators, and multiple recovery boilers. Complex mills are usually older mills that have been modernized and expanded. These classifications are independent of pulp production capacity because the complexity of a mill is most often the primary factor that drives investment costs for the installation of spent pulping liquor spill prevention and control systems.

For each level of mill complexity, EPA determined the types of equipment necessary to operate effective spill control systems. This equipment included liquor collection sumps, liquor storage capacity, fiber reclaim tanks, process area curbing and diking, turpentine and soap containment for kraft mills that process softwood, conductivity monitoring and high-level tank alarms, and costs for engineering analyses, initial BMP Plan preparation, and operator training. Based on information obtained from mill visits and the results of the NCASI BMP survey, EPA determined that single line kraft mills will require up to five liquor collection sumps (relatively small 4'×4'×4' or 4'×4'×8' concrete sumps equipped with conductivity-actuated liquor recovery pumps). Moderately complex mills will require up to 9 sumps, and complex mills will require up to 12 sumps. Each type of mill was assigned one 500,000-gallon spent pulping liquor storage

tank for the collection of recovered liquor. One fiber reclaim tank was assigned for single line mills, and two fiber reclaim tanks were assigned for the moderately complex and complex mills. The amount of process area curbing and diking, conductivity monitoring, turpentine and soap containment, and engineering analyses for initial BMP Plan preparation required for each type of mill was a function of the mill complexity. A similar process was followed for sulfite mills; however, there are no sulfite mills with more than one line.

Table 9-2 presents a summary of estimated BMP investment costs for kraft mills to fully implement effective spent pulping liquor spill prevention and control systems and containment measures for soap and turpentine. Table 9-3 presents similar information for sulfite mills. These cost estimates were prepared assuming the mills had no spill control equipment in place. The total investment costs for each type of mill are summarized below:

Type of Mill	Kraft Mill Investment Costs	Sulfite Mill Investment Costs
Single Line Mills	\$ 2,150,000	\$ 1,300,000
Moderately Complex Mills	\$ 3,250,000	None
Complex Mills	\$ 4,050,000	None

Based on information obtained from mill visits, NCASI BMP questionnaire responses, and reports in the literature, EPA determined that the following items contribute to the annual costs for implementing spent pulping liquor BMPs:

- Evaporation of recovered liquor;
- Operation and maintenance of new equipment;
- Tank integrity testing program; and
- Operator training.

The BMP implementation items that contributed to annual cost savings at the mills were as follows:

- Recovered fiber;
- Recovered pulping chemicals;
- Recovered energy; and
- Reduced wastewater treatment costs for power, nutrient addition, and sludge disposal.

Most mill operators did not complete the cost sections of the NCASI BMP questionnaires. The operators who did complete this section generally show a net annual cost savings from implementation of spent pulping liquor BMPs of \$0.20 to \$1.00 per ton of brownstock pulp. A few mills reported net annual costs ranging from \$0.01 to \$0.35 per ton of brownstock pulp. A few available reports and other sources of cost data for spent pulping liquor BMP implementation show annual net cost savings in the range of \$500,000 to \$750,000, and payback periods of less than 4 to 8 years (19,29).

9.3 Costs and Effluent Reductions - Mill Case Studies

Case studies of cost and effluent reductions resulting from spent pulping liquor BMP implementation at two bleached papergrade kraft mills are presented below. The first case study also provides anecdotal evidence supporting the need for adequate containment of turpentine as a part of an effective BMP program.

9.3.1 Southern U.S. Bleached Papergrade Kraft Mill

Table 9-4 and Figures 9-1 through 9-5 show the impacts of pulping liquor BMPs implemented at a southern kraft mill that pulps southern pine and discharges process wastewaters to an adjacent POTW (19). The process wastewater discharge from the mill accounts for more than 95% of the POTW influent flow. The mill has no on-site wastewater treatment facilities, and prior to 1991, had virtually no pulping liquor spill prevention and control facilities. Primary and secondary wastewater treatment have been provided by the POTW. From 1990 to 1991, the mill installed an extensive pulping liquor spill prevention and control system for black liquor, green liquor, white liquor, and lime mud. The system includes several process area liquor collection sumps and refurbished oil storage tanks that are used to collect pulping liquor. The mill also partially closed a screen room. Relatively minor operational changes were also instituted at the POTW during that period; however, the POTW was not upgraded in terms of additional unit operations or additional treatment capacity.

The first full year of operation of the black liquor spill prevention and control system at the mill was 1992. Production of brownstock pulp during 1992 was about 6% less than that for 1988. The annual average POTW effluent flow for 1992 was less than 3% lower than the 1988 annual average, but about 3% higher when normalized to pulp production. Although there was little change in the total mill wastewater volume resulting from the BMPs (on an average basis), maximum flows to the POTW were reduced, and there was a marked decrease in the variation in the effluent flow. Table 9-4 presents a tabular summary of the changes in the mill's effluent as a result of the black pulping liquor BMP implementation. Figure 9-1 depicts the reduced wastewater flow to the POTW that occurred after the BMP implementation.

The distribution of POTW influent COD data presented on Figure 9-2 shows a marked reduction in POTW COD influent loadings. In particular, the 80th percentile to the maximum value COD loadings were lower after spent pulping liquor controls were implemented. The overall reduction in the average BOD₅ influent loadings was about 20%. POTW effluent data for COD, TSS, and BOD₅, normalized to annual pulp mill production, showed significant reductions in 95th percentile effluent mass loadings (see Figures 9-3 through 9-5 and Table 9-4).

The reductions in the annual average effluent mass loadings for COD, TSS, and BOD₅ were 27%, 57%, and 17%, respectively. The most significant reductions were at the higher percentile mass loadings, suggesting that effective spent pulping liquor controls reduced short-term adverse impacts on POTW operations. The reductions in effluent loading were not always associated with reductions in maximum flows. Although the average POTW influent COD loading was reduced by 22%, the average POTW effluent loading was reduced by 27%. These results suggest that the spent pulping liquor controls resulted in removal of a greater portion of COD material from pulping liquor that is refractory to conventional biological treatment.

The mill had a spill of turpentine during May 1992, which impacted POTW performance for late May and part of June 1992. Although not discernable on Figures 9-3 through 9-5, the adverse impact of the spill resulted in the higher percentile mass loadings of COD, TSS, and BOD₅ shown on these figures. The impact of the spill is more clearly shown on Figure 9-6, which provides a time-series plot of seven-day average POTW effluent BOD₅ for 1992. These results clearly demonstrate the importance of providing proper containment for turpentine process areas and bulk storage tanks as part of a pulp mill BMP Plan. Had effective controls been in effect at the time of the spill, it could have been contained, and the adverse impacts on POTW operations (interference and pass-through) could have been avoided.

Whole effluent toxicity data reported by the POTW show that intermittent acute toxicity to *Daphnia* and *Pimephales promelas* was eliminated, as was intermittent chronic toxicity to

Pimephales promelas. Consistent chronic toxicity to *Daphnia* was substantially reduced, except during the period of the turpentine spill.

The mill's total investment costs for the spill prevention and control systems, including refurbishment of two fuel oil storage tanks, was about \$4 million dollars (1990-1991). The mill estimates that the net annual cost savings for recovery of black liquor at 3 to 4% liquor solids is about \$500,000, excluding the cost savings for recovered fiber, which have not been measured or estimated. The costs incurred at this mill are in line with those presented in Table 9-2 for BMPs for control of spent pulping liquor, if they are adjusted upward about \$500,000 to \$750,000 to account for additional controls for white liquor, green liquor, and lime mud.

9.3.2 Canadian Bleached Papergrade Kraft Mill

Another BMP implementation case study involves a Canadian bleached kraft mill with two fiberlines. The No. 1 pulp mill began operations during 1948 and is now dedicated to hardwoods, principally aspen. The No. 2 pulp mill began operations during 1978 and processes mainly black spruce (29,30). The spent pulping liquor spill prevention and control system was installed in response to a control order issued by the Ontario Ministry of Environment before the installation of secondary treatment in 1987. Spent pulping liquor spill prevention and control was identified as the highest-priority project for reducing final effluent toxicity at the mill (29,30).

The major elements of the upgraded spill prevention and control system were:

- Reactivation of the original pulp mill spill tank;
- Installation of a new 120,000-gallon spill tank;
- Installation of a conductivity-activated sump in the No. 2 pulp mill, and routing of gland water and decker white water around the sump;

9.0 Estimated Costs and Effluent Reduction Benefits

- Prevention of softwood fibers from entering the No. 1 pulp mill's hardwood line;
- Collection of spilled spent pulping liquor in as concentrated a form as possible;
- Upgrading of the sewer monitoring network; and
- Development of a computer monitoring system for 15 wastewater streams and 37 tanks and vessels.

The capital cost for the upgraded spill prevention and control system was reported at \$2,400,000 (1985 Canadian dollars) (29,30). The net annual operating savings were reported as follows (1985 Canadian dollars):

Savings in Recovered Chemicals	\$700,000
Savings in Recovered Fiber	250,000
Cost of Extra Evaporation of Recovered Liquor	<u>(200,000)</u>
Net Annual Savings	\$750,000

From these data, EPA estimated a return on investment of 31% and a payback period of 3.2 years. Mill operators reported that the break-even point for the recovery of dilute black liquor is about 4% liquor solids, and that recovery of very dilute liquors (less than 2% liquor solids) is avoided by collecting spilled or lost liquor before its dilution with other wastewaters (29,30).

The effluent reduction benefits experienced by the Canadian bleached kraft mill are described in Table 9-5. The operators at this mill attributed these effluent reduction benefits to the upgraded spent pulping liquor controls. The effluent reduction benefits were attained before the installation of an aerated stabilization basin that was completed during 1989 (29,30).

9.4 General Conclusions

Based on the results of these case studies and on other information presented in this report, EPA believes that improved management of spent pulping liquor, soap, and turpentine and effective spill prevention and control can result in the following effluent reduction benefits:

- Reduced mass loadings of priority, non-conventional, and conventional pollutants in untreated wastewaters, and reduced toxicity of raw waste loadings prior to biological treatment;
- Reduced toxicity in biologically treated pulp mill effluents;
- Reduced wastewater flows and discharges of priority, non-conventional, and conventional pollutants;
- Reduced potential for catastrophic spills of spent pulping liquor, soap, and turpentine directly into waterways; and
- Reduced potential for upsets to wastewater treatment facilities from in-mill spills, and reduced potential for increased discharges of unchlorinated and chlorinated toxic compounds, effluent toxicity, and conventional and non-conventional pollutants (BOD₅, COD, and TSS) associated with treatment system upsets.

Non-water quality environmental impacts from improved spent pulping liquor control systems include:

- Reduced incidental emissions of volatile HAPs, including methanol and methyl ethyl ketone;
- For kraft mills, reduced incidental atmospheric emissions of odor-causing TRS compounds, including hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide;
- Improved energy efficiency resulting from the combustion of black liquor solids that would otherwise be lost to the sewer (a net increase in energy use will occur if very dilute weak liquors are processed);
- Improved process efficiency, including a reduced need for make-up chemicals and more efficient utilization of operating and supervisory personnel; and

- Reduced environmental impacts associated with the manufacture and transportation of make-up chemicals no longer required at the pulp mill because of increased spent pulping liquor recovery.

For a typical kraft mill with no BMPs in place, EPA estimates that the average incremental untreated wastewater BOD₅ loading reduction attainable from effective black liquor spill prevention and control is about 5 kg/ADMT of brownstock pulp (2). Accordingly, for mills with adequate black liquor spill prevention and control programs, there will be no incremental untreated wastewater BOD₅ loading reduction, and only limited incremental costs for preparation of the BMP Plan and minor facility upgrades. For mills with marginally adequate programs, EPA estimates that the average incremental untreated wastewater BOD₅ loading reduction will be about 2.5 kg/ADMT. For mills with inadequate programs, the estimated average incremental untreated BOD₅ loading reduction will be about 5 kg/ADMT. For sulfite mills, EPA assigned effluent average loading reductions of 2.5 kg/ADMT for half of the mills, and 5 kg/ADMT for the other half of the mills. The reduction in untreated wastewater BOD₅ loadings will, in turn, result in reduced effluent loadings.

EPA's conclusions regarding spent pulping liquor management and BMP implementation are as follows:

- Spent pulping liquor management and spill control systems, as well as spill control systems for other chemicals such as turpentine and soap, are important for economic operation of kraft pulping and recovery systems, for minimizing adverse impacts on wastewater treatment systems, and for producing optimum effluent quality. Such systems are essential for minimizing effluent discharges from chemical pulp mills.
- Spent pulping liquor management and control systems are best implemented through a combination of spent pulping liquor management systems and operating practices (non-hardware) and spill collection and recovery systems (hardware). Spill and loss prevention, rather than spill collection, is essential for effective spent pulping liquor management.

9.0 Estimated Costs and Effluent Reduction Benefits

- Approximately 26% of the bleached kraft and soda mills in the United States have essentially complete spent pulping liquor management and control systems, approximately 29% have partial systems, and approximately 45% would require major upgrades to fully implement effective control systems. Sulfite mills in the United States are estimated to have a status similar to the bleached kraft mills.
- Collection and recovery of kraft black liquor at liquor solids concentrations of 3 to 4% will be cost-effective at most kraft mills. Consequently, emphasis must be placed on collecting spent liquor at concentrations greater than 3 to 4%. This is achieved by strategically locating sumps, curbs and other diversion and collection systems so that the spent liquor is recovered prior to mixing with wastewaters or already diluted spent liquor. Some mills collect and recover spent liquor at lower liquor solids concentrations because of effluent color considerations. Evaporator hydraulic capacity is likely to be a limiting factor that either will prevent many mills from recovering spent pulping liquor at low liquor solids concentrations or require upgrades to evaporators and/or appurtenant equipment to meet local requirements (e.g., color limits).
- Two case studies show that for mills with few spent pulping liquor control systems in place, liquor spill prevention and control can be cost-effective. The return on investment may not be exceptionally high; however, substantial cost savings could occur at mills where effective spent pulping liquor management and spill control systems can be installed instead of effluent color treatment systems or upgraded biological treatment systems.
- Additional benefits associated with effective spent pulping liquor management that cannot be quantified include: a cleaner internal mill environment for mill staff, and a cleaner receiving water environment resulting from reduced effluent discharges, reduced secondary environmental impacts achieved through the use of recovered chemicals, and reduced risk of effluent limitation exceedances.

Table 9-1

**BMP Implementation Status for Spent Pulping Liquor Control Systems at
Bleached Kraft and Soda Mills, and Sulfite Mills**

Pulping Process	BMP Implementation Status		
	Number of Mills in Category 1 (10 % costs)	Number of Mills in Category 2 (up to 60 % costs)	Number of Mills in Category 3 (up to 90 % costs)
Bleached Kraft and Soda	22	25	37
Dissolving Kraft	1	0	2
Total	23	25	39
Papergrade Sulfite	3	3	5
Dissolving Sulfite	0	2	2
Total	3	5	7

Sources: EPA Mill Visit Reports
NCASI, 1994 (23)
AF&PA, 1995 (24)

Table 9-2

**BMP Investment Cost Estimates for Bleached Papergrade Kraft
and Soda Mills**

EPA Model BMP Technology	Mill Complexity		
	Single Line	Moderately Complex	Complex
Liquor Collection Sumps	\$750,000 (up to 5 sumps)	\$1,350,000 (up to 9 sumps)	\$1,800,000 (up to 12 sumps)
Liquor Storage Capacity (one 500,000-gallon tank)	600,000	600,000	600,000
Fiber Reclaim Tank(s)	150,000 (one tank)	300,000 (two tanks)	300,000 (two tanks)
Process Area Curbing and Diking	200,000	300,000	400,000
Turpentine and Soap Containment	150,000	250,000	350,000
Sewer Conductivity Monitoring and Storage Tank Alarms	150,000	250,000	350,000
Initial BMP Plan Preparation and Initial Operator Training	150,000	200,000	250,000
Total	\$2,150,000	\$3,250,000	\$4,050,000

Note: Derived from EPA Mill Site Visit Reports, EPA project files and Reference 23.

Table 9-3**BMP Investment Cost Estimates for Papergrade Sulfite Mills**

EPA Model BMP Technology	Single Line
Liquor Collection Sumps	\$450,000 (up to 3 sumps)
Liquor Storage Capacity (one 200,000-gallon tank)	300,000
Fiber Reclaim Tank	150,000
Process Area Curbing and Diking	150,000
Sewer Conductivity Monitoring and Storage Tank Alarms	100,000
Initial BMP Plan Preparation and Initial Operator Training	150,000
Total	\$1,300,000

*Note: All sulfite mills have a single fiber line.
Derived from EPA Mill Visit Reports, EPA project files, and Reference 23.*

Table 9-4

**Effects of Spent Pulping Liquor Control Systems on POTW Effluent Quality
at a Southern U.S. Bleached Papergrade Kraft Mill Discharging to POTW**

POTW Effluent Characteristic	1988 Effluent Quality	1992 Effluent Quality	Percent Change
Flow (m³/ADMT)			
95th Percentile	154	140	
Median	120	127	+ 5.8
Mean	117	121	+ 3.4
Standard Deviation	24.2	17.9	
Coefficient of Variation	0.21	0.15	- 29
COD (kg/ADMT)			
95th Percentile	54.7	41.1	
Median	37.3	26.9	- 28
Mean	37.7	27.6	- 27
Standard Deviation	10.8	8.52	
Coefficient of Variation	0.29	0.31	+ 6.8
TSS (kg/ADMT)			
95th Percentile	10.4	5.08	
Median	5.11	2.15	- 58
Mean	5.61	2.41	- 57
Standard Deviation	2.93	1.30	
Coefficient of Variation	0.52	0.54	+ 3.8
BOD₅ (kg/ADMT)			
95th Percentile	4.23	3.65	
Median	1.90	1.49	- 23
Mean	2.09	1.73	- 17
Standard Deviation	1.14	1.04	
Coefficient of Variation	0.55	0.60	+ 9.0

Source: EPA, 1993 (19)

Table 9-5

**Quantified Effluent Reduction Benefits From Spent Pulping
Liquor Control System at a Kraft Mill Without Secondary Treatment**

Effluent Characteristic	March 1982	July 1985	Percent Reduction
Flow (m ³ /adt)	135	106	21 %
BOD (kg/adt)	40	29	27 %
TSS (kg/adt)	8.6	5.3	38 %
Dissolved Solids (kg/adt)	200	145	27 %
Sodium (kg Na ₂ SO ₄ /adt)	146	108	26 %
Toxic Contribution (TU m ³ /adt)	1,060	335	68 %

*Note: TU - Toxic units calculated as the reciprocal of the LC₅₀ using static bioassays multiplied by 100. Toxic units were converted to toxic contribution in m³/admt by multiplying the toxic units by the flow of the effluent and dividing by mill production. Bioassays were conducted using juvenile rainbow trout (*Salmo gairdneri*).*

Sources: Scroggins, 1986 (29)
Sikes and Almost, 1986 (30)

Figure 9-1

Effect of Spent Pulping Liquor Control Systems on POTW Effluent Flow at a Kraft Mill

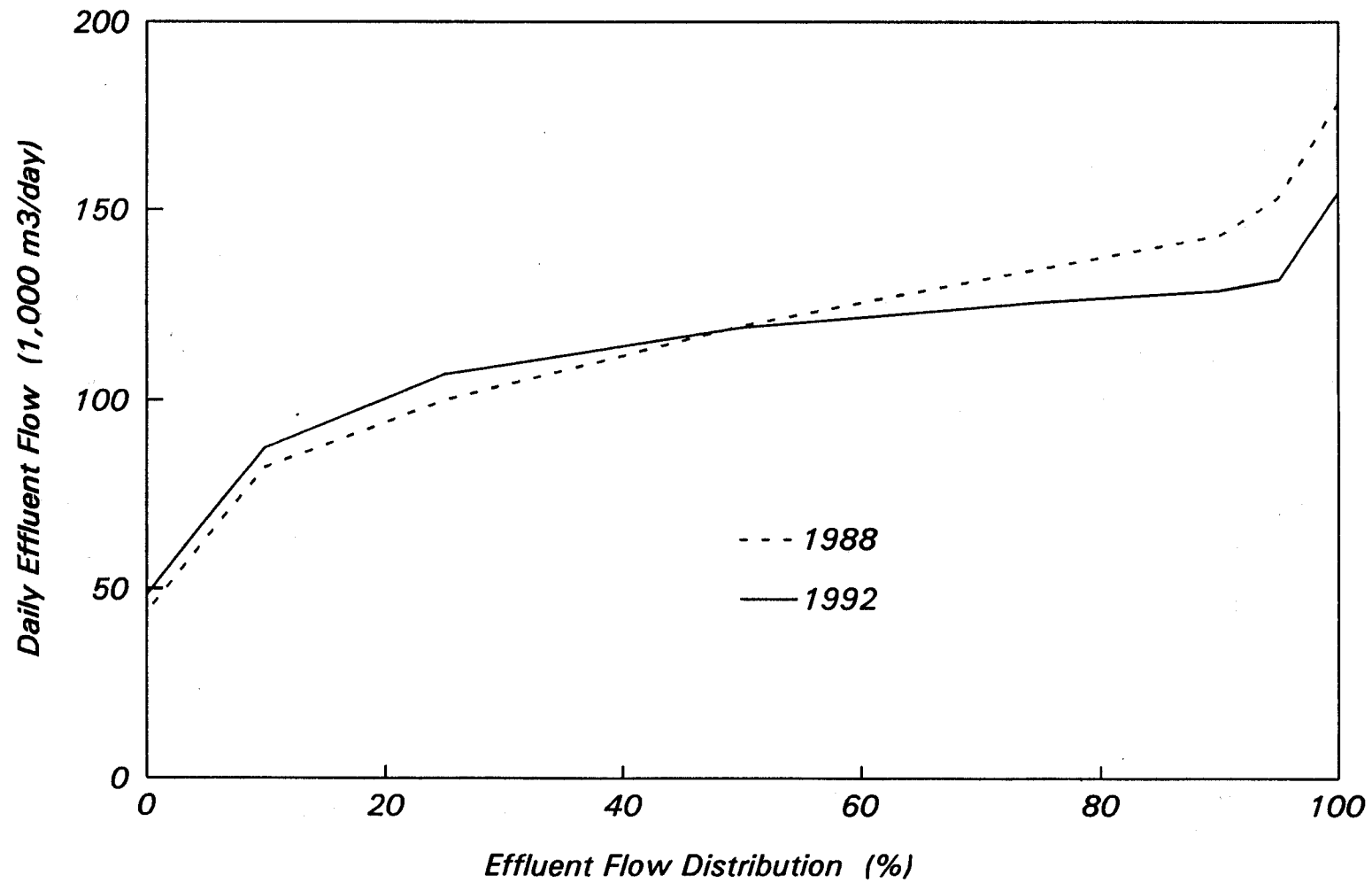


Figure 9-2

Effect of Spent Pulping Liquor Control Systems on POTW Influent COD Levels at a Kraft Mill

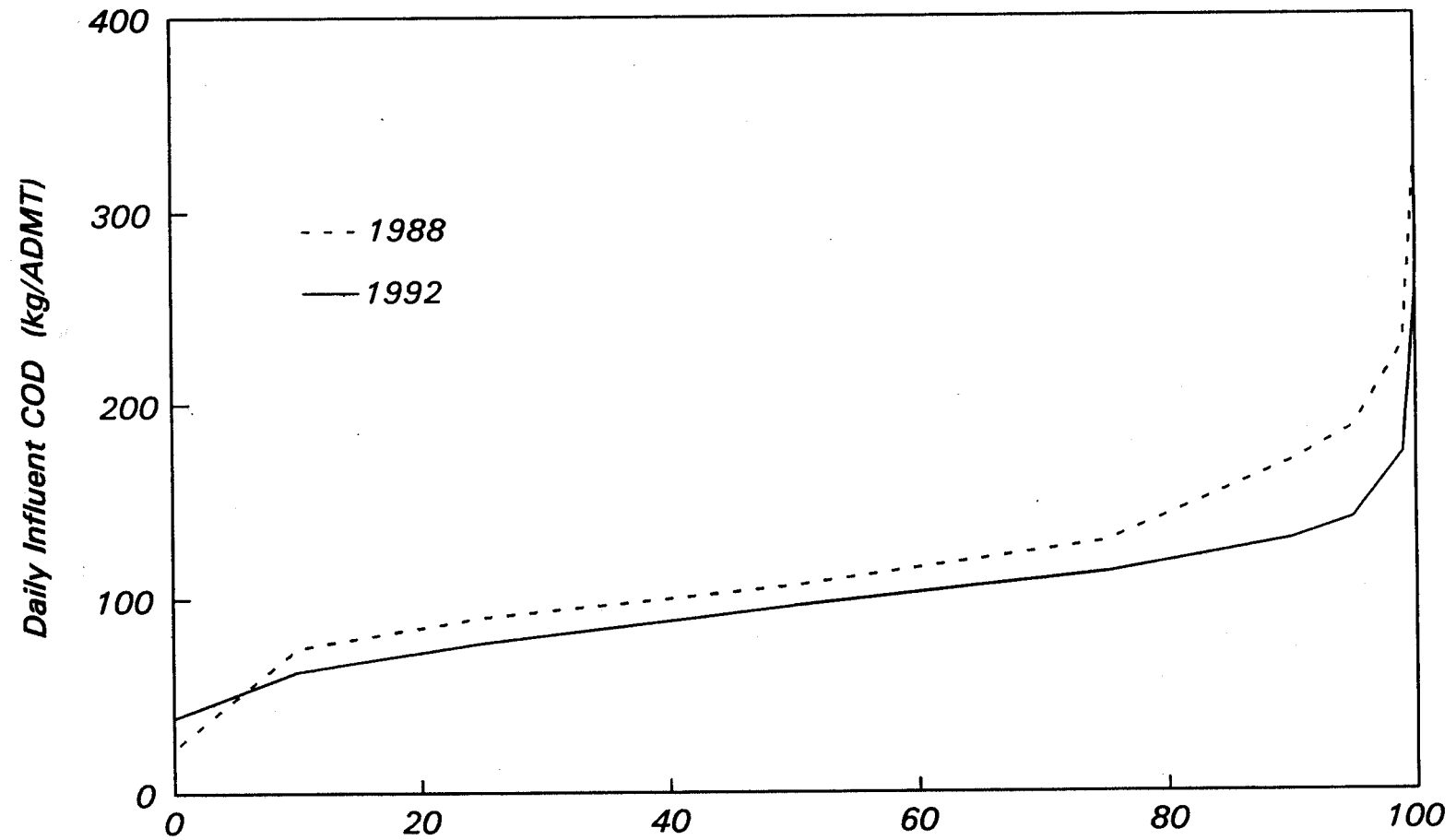


Figure 9-3

Effect of Spent Pulping Liquor Control Systems on POTW Effluent COD Levels at a Kraft Mill

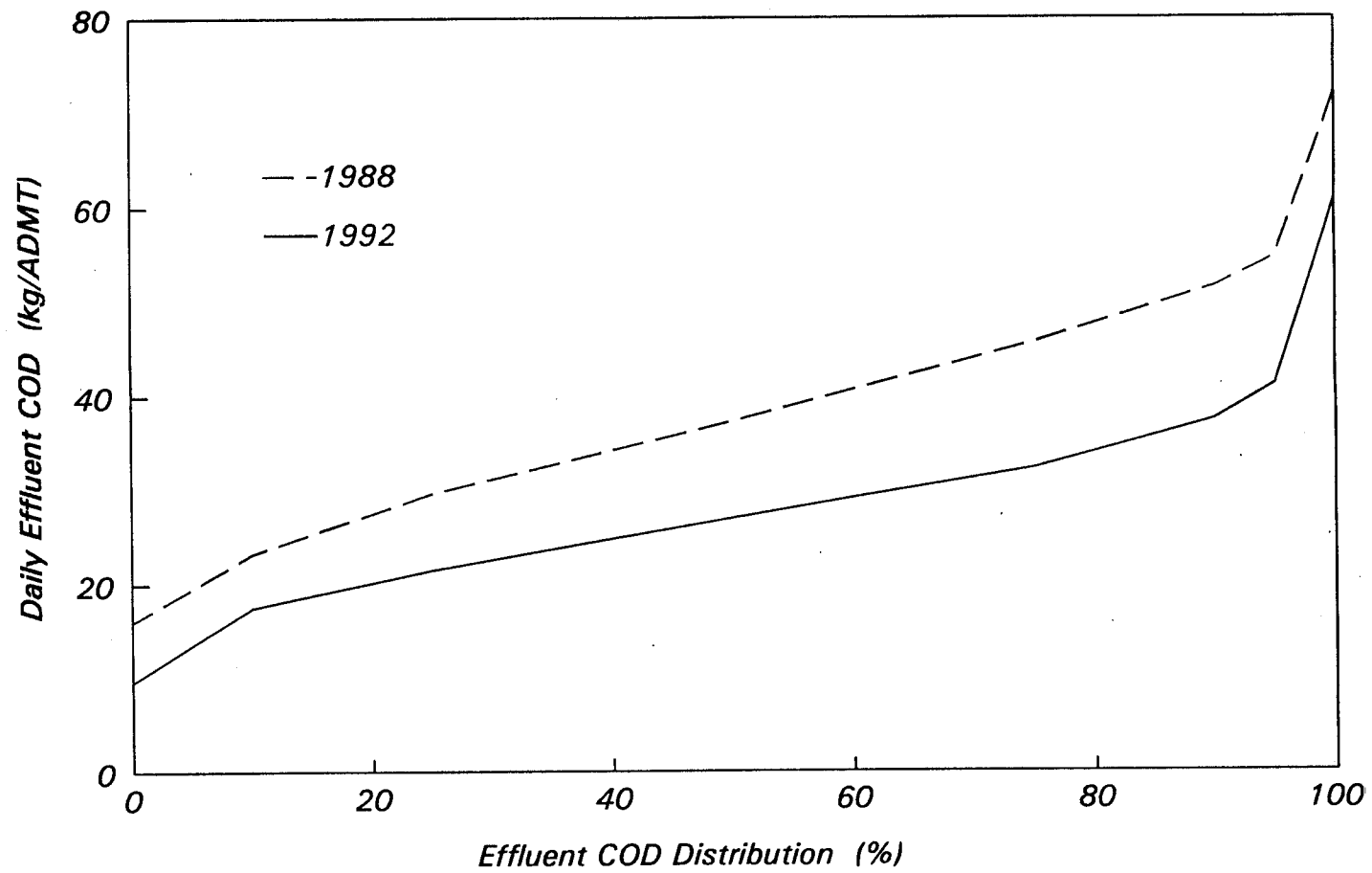


Figure 9-4

Effect of Spent Pulping Liquor Control Systems on TSS Levels at a Kraft Mill

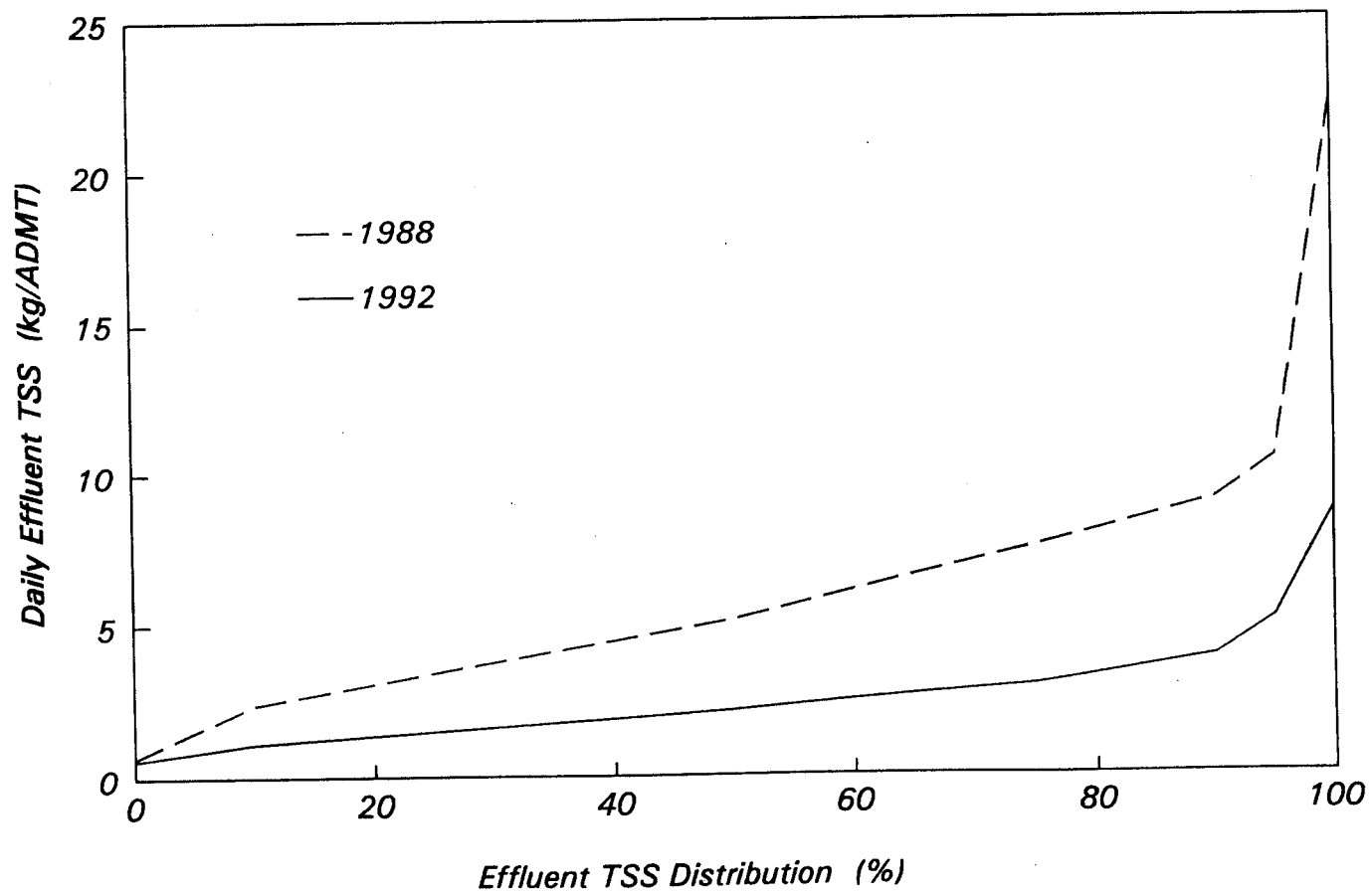


Figure 9-5

Effect of Spent Pulping Liquor Control Systems on BOD₅ Levels at a Kraft Mill

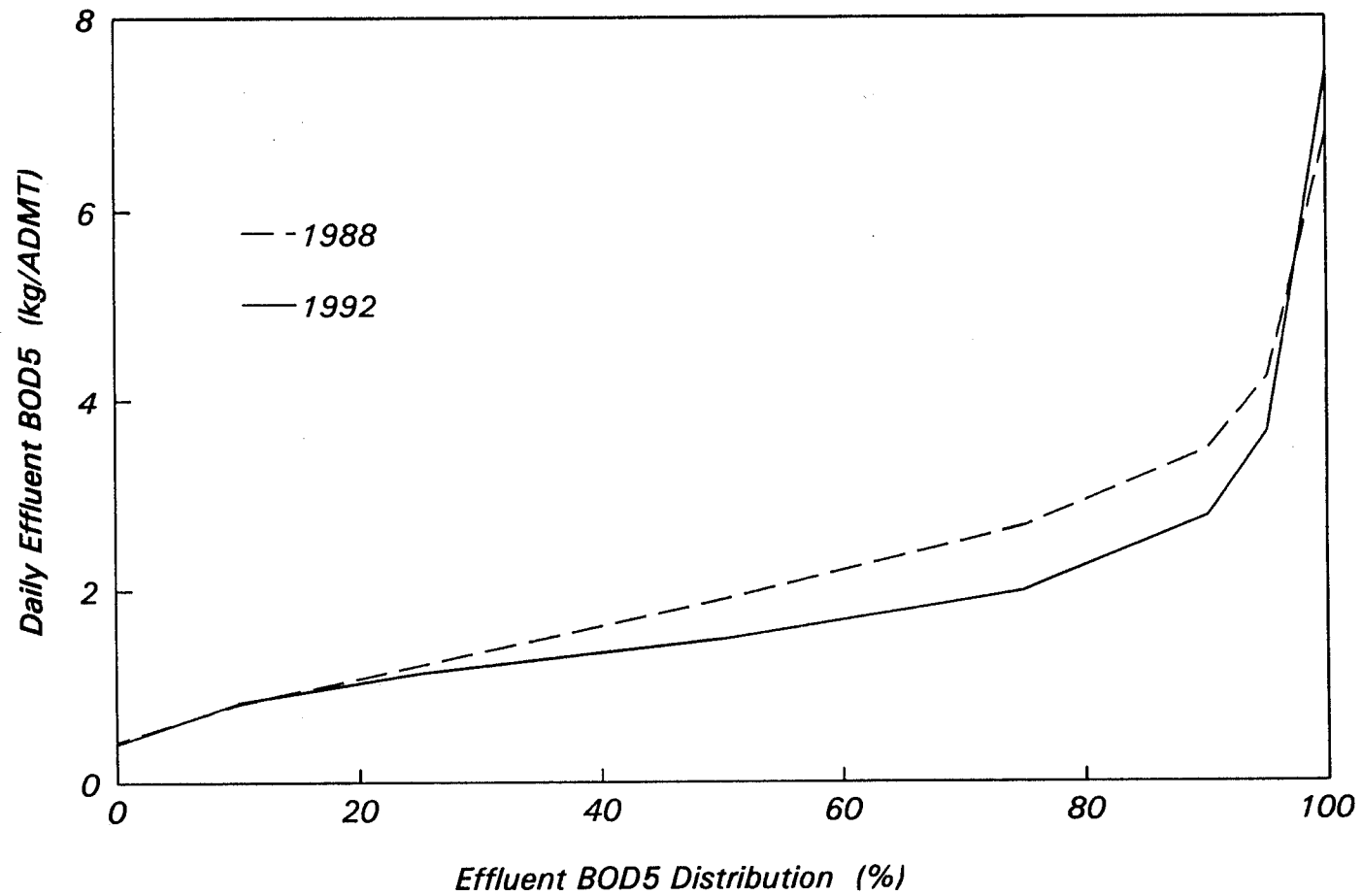
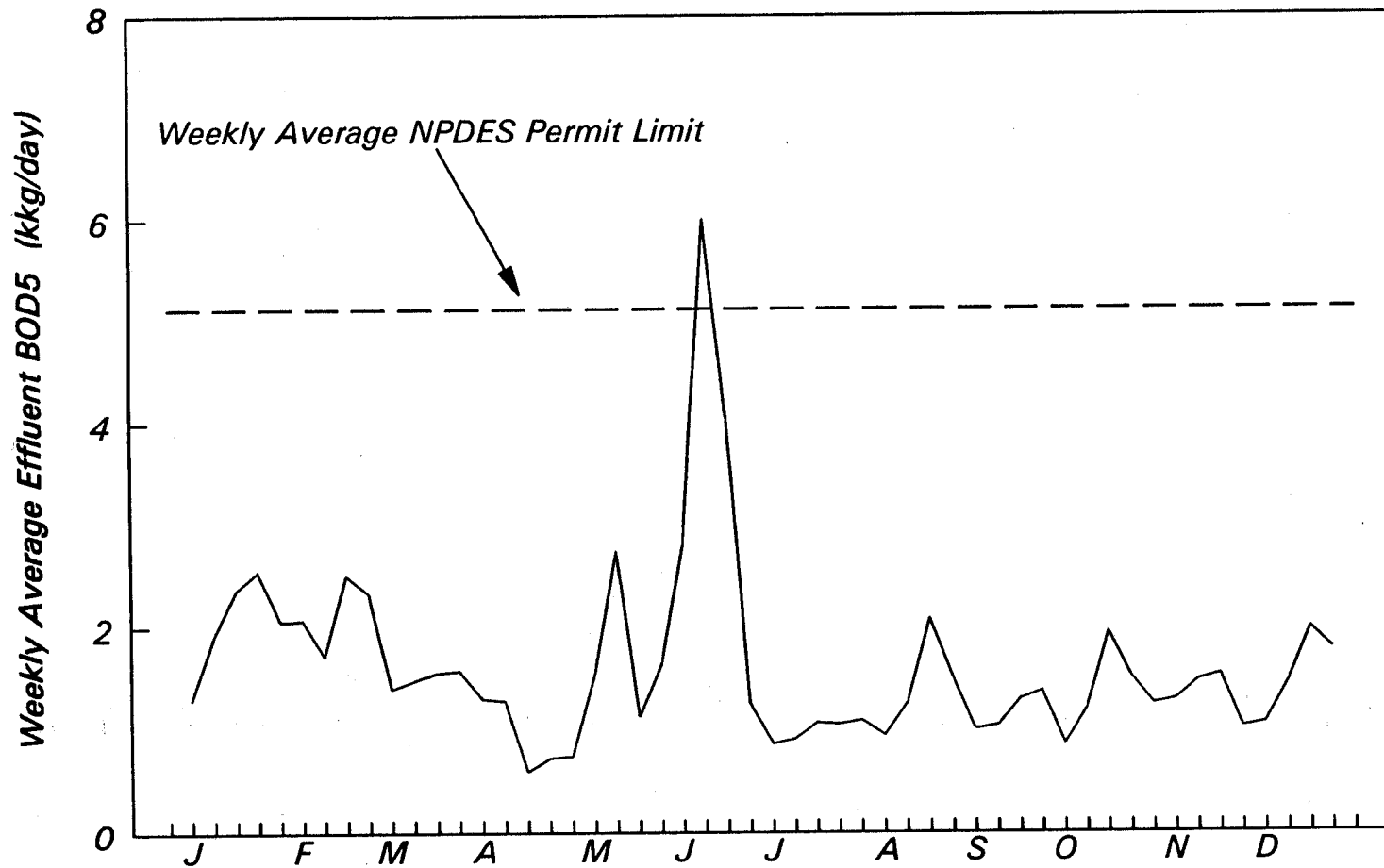


Figure 9-6

Effect of a Major Turpentine Spill at a Kraft Mill on Effluent BOD₅



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ATTACHMENT A
BEST MANAGEMENT PRACTICES REGULATION

§430.03 Best Management Practices for spent pulping liquor, soap, and turpentine management, spill prevention, and control

(a) Applicability. This section applies to direct and indirect discharging pulp, paper, and paperboard mills with pulp production in Subparts B (Bleached Papergrade Kraft and Soda) and E (Papergrade Sulfitite).

(b) Specialized definitions. (1) Action Level: A daily pollutant loading that when exceeded triggers investigative or corrective action. Mills determine action levels by a statistical analysis of six months of daily measurements collected at the mill. For example, the lower action level may be the 75th percentile of the running seven-day averages (that value exceeded by 25 percent of the running seven-day averages) and the upper action level may be the 90th percentile of the running seven-day averages (that value exceeded by 10 percent of the running seven-day averages).

(2) Equipment Items in Spent Pulping Liquor, Soap, and Turpentine Service: Any process vessel, storage tank, pumping system, evaporator, heat exchanger, recovery furnace or boiler, pipeline, valve, fitting, or other device that contains, processes, transports, or comes into contact with spent pulping liquor, soap, or turpentine. Sometimes referred to as “equipment items.”

(3) Immediate Process Area: The location at the mill where pulping, screening, knotting, pulp washing, pulping liquor concentration, pulping liquor processing, and chemical recovery facilities are located, generally the battery limits of the aforementioned processes. “Immediate process area” includes spent pulping liquor storage and spill control tanks located at the mill, whether or not they are located in the immediate process area.

(4) Intentional Diversion: The planned removal of spent pulping liquor, soap, or turpentine from equipment items in spent pulping liquor, soap, or turpentine service by the mill for any purpose including, but not limited to, maintenance, grade changes, or process shutdowns.

(5) Mill: The owner or operator of a direct or indirect discharging pulp, paper, or paperboard manufacturing facility subject to this section.

(6) Senior Technical Manager: The person designated by the mill manager to review the BMP Plan. The senior technical manager shall be the chief engineer at the mill, the manager of pulping and chemical recovery operations, or other such responsible person designated by the

mill manager who has knowledge of and responsibility for pulping and chemical recovery operations.

(7) Soap: The product of reaction between the alkali in kraft pulping liquor and fatty acid portions of the wood, which precipitate out when water is evaporated from the spent pulping liquor.

(8) Spent Pulping Liquor: For kraft and soda mills “*spent pulping liquor*” means black liquor that is used, generated, stored, or processed at any point in the pulping and chemical recovery processes. For sulfite mills “*spent pulping liquor*” means any intermediate, final, or used chemical solution that is used, generated, stored, or processed at any point in the sulfite pulping and chemical recovery processes (e.g., ammonium-, calcium-, magnesium-, or sodium-based sulfite liquors).

(9) Turpentine: A mixture of terpenes, principally pinene, obtained by the steam distillation of pine gum recovered from the condensation of digester relief gases from the cooking of softwoods by the kraft pulping process. Sometimes referred to as sulfate turpentine.

(c) Requirement to implement Best Management Practices. Each mill subject to this section must implement the Best Management Practices (BMPs) specified in paragraphs (1) through (10) of this section. The primary objective of the BMPs is to prevent leaks and spills of spent pulping liquors, soap, and turpentine. The secondary objective is to contain, collect, and recover at the immediate process area, or otherwise control, those leaks, spills, and intentional diversions of spent pulping liquor, soap, and turpentine that do occur. BMPs must be developed according to best engineering practices and must be implemented in a manner that takes into account the specific circumstances at each mill. The BMPs are as follows:

(1) The mill must return spilled or diverted spent pulping liquors, soap, and turpentine to the process to the maximum extent practicable as determined by the mill, recover such materials outside the process, or discharge spilled or diverted material at a rate that does not disrupt the receiving wastewater treatment system.

(2) The mill must establish a program to identify and repair leaking equipment items. This program must include:

(i) Regular visual inspections (e.g., once per day) of process areas with equipment items in spent pulping liquor, soap, and turpentine service;

(ii) Immediate repairs of leaking equipment items, when possible. Leaking equipment items that cannot be repaired during normal operations must be identified, temporary means for mitigating the leaks must be provided, and the leaking equipment items repaired during the next maintenance outage;

(iii) Identification of conditions under which production will be curtailed or halted to repair leaking equipment items or to prevent pulping liquor, soap, and turpentine leaks and spills; and

(iv) A means for tracking repairs over time to identify those equipment items where upgrade or replacement may be warranted based on frequency and severity of leaks, spills, or failures.

(3) The mill must operate continuous, automatic monitoring systems that the mill determines are necessary to detect and control leaks, spills, and intentional diversions of spent pulping liquor, soap, and turpentine. These monitoring systems should be integrated with the mill process control system and may include, e.g., high level monitors and alarms on storage tanks; process area conductivity (or pH) monitors and alarms; and process area sewer, process wastewater, and wastewater treatment plant conductivity (or pH) monitors and alarms.

(4) The mill must establish a program of initial and refresher training of operators, maintenance personnel, and other technical and supervisory personnel who have responsibility for operating, maintaining, or supervising the operation and maintenance of equipment items in spent pulping liquor, soap, and turpentine service. The refresher training must be conducted at least annually and the training program must be documented.

(5) The mill must prepare a brief report that evaluates each spill of spent pulping liquor, soap, or turpentine that is not contained at the immediate process area and any intentional diversion of spent pulping liquor, soap, or turpentine that is not contained at the immediate process area. The report must describe the equipment items involved, the circumstances leading to the incident, the effectiveness of the corrective actions taken to contain and recover the spill or intentional diversion, and plans to develop changes to equipment and operating and maintenance practices as necessary to prevent recurrence. Discussion of the reports must be included as part of the annual refresher training.

(6) The mill must establish a program to review any planned modifications to the pulping and chemical recovery facilities and any construction activities in the pulping and chemical recovery areas before these activities commence. The purpose of such review is to prevent leaks and spills of spent pulping liquor, soap, and turpentine during the planned modifications, and to ensure that construction and supervisory personnel are aware of possible liquor diversions and of the requirement to prevent leaks and spills of spent pulping liquors, soap, and turpentine during construction.

(7) The mill must install and maintain secondary containment (i.e., containment constructed of materials impervious to pulping liquors) for spent pulping liquor bulk storage tanks equivalent to the volume of the largest tank plus sufficient freeboard for precipitation. An annual tank integrity testing program, if coupled with other containment or diversion structures, may be substituted for secondary containment for spent pulping liquor bulk storage tanks.

(8) The mill must install and maintain secondary containment for turpentine bulk storage tanks.

(9) The mill must install and maintain curbing, diking or other means of isolating soap and turpentine processing and loading areas from the wastewater treatment facilities.

(10) The mill must conduct wastewater monitoring to detect leaks and spills, to track the effectiveness of the BMPs, and to detect trends in spent pulping liquor losses. Such monitoring must be performed in accordance with paragraph (i) of this section.

(d) Requirement to develop a BMP Plan. (1) Each mill subject to this section must prepare and implement a BMP Plan. The BMP Plan must be based on a detailed engineering review as described in paragraphs (d)(2) and (3) of this section. The BMP Plan must specify the procedures and the practices required for each mill to meet the requirements of paragraph (c) of this section, the construction the mill determines is necessary to meet those requirements including a schedule for such construction, and the monitoring program (including the statistically derived action levels) that will be used to meet the requirements of paragraph (i) of this section. The BMP Plan also must specify the period of time that the mill determines the action levels established under paragraph (h) of this section may be exceeded without triggering the responses specified in paragraph (i) of this section.

(2) Each mill subject to this section must conduct a detailed engineering review of the pulping and chemical recovery operations -- including but not limited to process equipment, storage tanks, pipelines and pumping systems, loading and unloading facilities, and other appurtenant pulping and chemical recovery equipment items in spent pulping liquor, soap, and turpentine service -- for the purpose of determining the magnitude and routing of potential leaks, spills, and intentional diversions of spent pulping liquors, soap, and turpentine during the following periods of operation:

- (i) Process start-ups and shut downs;
- (ii) Maintenance;
- (iii) Production grade changes;
- (iv) Storm or other weather events;
- (v) Power failures; and
- (vi) Normal operations.

(3) As part of the engineering review, the mill must determine whether existing spent pulping liquor containment facilities are of adequate capacity for collection and storage of anticipated intentional liquor diversions with sufficient contingency for collection and containment of spills. The engineering review must also consider:

(i) The need for continuous, automatic monitoring systems to detect and control leaks and spills of spent pulping liquor, soap, and turpentine;

(ii) The need for process wastewater diversion facilities to protect end-of-pipe wastewater treatment facilities from adverse effects of spills and diversions of spent pulping liquors, soap, and turpentine;

(iii) The potential for contamination of storm water from the immediate process areas; and

(iv) The extent to which segregation and/or collection and treatment of contaminated storm water from the immediate process areas is appropriate.

(e) Amendment of BMP Plan. (1) Each mill subject to this section must amend its BMP Plan whenever there is a change in mill design, construction, operation, or maintenance that materially affects the potential for leaks or spills of spent pulping liquor, turpentine, or soap from the immediate process areas.

(2) Each mill subject to this section must complete a review and evaluation of the BMP Plan five years after the first BMP Plan is prepared and, except as provided in paragraph (e)(1) of this section, once every five years thereafter. As a result of this review and evaluation, the mill must amend the BMP Plan within three months of the review if the mill determines that any new or modified management practices and engineered controls are necessary to reduce significantly the likelihood of spent pulping liquor, soap, and turpentine leaks, spills, or intentional diversions from the immediate process areas, including a schedule for implementation of such practices and controls.

(f) Review and certification of BMP Plan. The BMP Plan, and any amendments thereto, must be reviewed by the senior technical manager at the mill and approved and signed by the mill manager. Any person signing the BMP Plan or its amendments must certify to the permitting or pretreatment control authority under penalty of law that the BMP Plan (or its amendments) has been prepared in accordance with good engineering practices and in accordance with this regulation. The mill is not required to obtain approval from the permitting or pretreatment control authority of the BMP Plan or any amendments thereto.

(g) Record keeping requirements. (1) Each mill subject to this section must maintain on its premises a complete copy of the current BMP Plan and the records specified in paragraph (2) of this section and must make such BMP Plan and records available to the permitting or pretreatment control authority and the Regional Administrator or his or her designee for review upon request.

(2) The mill must maintain the following records for three years from the date they are created:

(i) Records tracking the repairs performed in accordance with the repair program described in paragraph (c)(2) of this section;

(ii) Records of initial and refresher training conducted in accordance with paragraph (c)(4) of this section;

(iii) Reports prepared in accordance with paragraph (c)(5) of this section; and

(iv) Records of monitoring required by paragraphs (c)(10) and (i) of this section.

(h) Establishment of wastewater treatment system influent action levels. (1) Each mill subject to this section must conduct a monitoring program, described in paragraph (2) of this

section, for the purpose of defining wastewater treatment system influent characteristics (or action levels), described in paragraph (3) of this section, that will trigger requirements to initiate investigations on BMP effectiveness and to take corrective action.

(2) Each mill subject to this section must employ the following procedures in order to develop the action levels required by paragraph (h) of this section:

(i) Monitoring parameters. The mill must collect 24-hour composite samples and analyze the samples for a measure of organic content (e.g., Chemical Oxygen Demand (COD) or Total Organic Carbon (TOC)). Alternatively, the mill may use a measure related to spent pulping liquor losses measured continuously and averaged over 24 hours (e.g., specific conductivity or color).

(ii) Monitoring locations. For direct dischargers, monitoring must be conducted at the point influent enters the wastewater treatment system. For indirect dischargers monitoring must be conducted at the point of discharge to the POTW. For the purposes of this requirement, the mill may select alternate monitoring point(s) in order to isolate possible sources of spent pulping liquor, soap, or turpentine from other possible sources of organic wastewaters that are tributary to the wastewater treatment facilities (e.g., bleach plants, paper machines and secondary fiber operations).

(3) By the date prescribed in paragraph (j)(1)(iii) of this section, each existing discharger subject to this section must complete an initial six-month monitoring program using the procedures specified in paragraph (h)(2) of this section and must establish *initial action levels* based on the results of that program. A wastewater treatment influent action level is a statistically determined pollutant loading determined by a statistical analysis of six months of daily measurements. The action levels must consist of a *lower action level*, which if exceeded will trigger the investigation requirements described in paragraph (i) of this section, and an *upper action level*, which if exceeded will trigger the corrective action requirements described in paragraph (i) of this section.

(4) By the date prescribed in paragraph (j)(1)(vi) of this section, each existing discharger must complete a second six-month monitoring program using the procedures specified in paragraph (h)(2) of this section and must establish *revised action levels* based on the results of

that program. The initial action levels shall remain in effect until replaced by revised action levels.

(5) By the date prescribed in paragraph (j)(2) of this section, each new source subject to this section must complete a six-month monitoring program using the procedures specified in paragraph (h)(2) of this section and must develop a *lower action level* and an *upper action level* based on the results of that program.

(6) Action levels developed under this paragraph must be revised using six months of monitoring data after any change in mill design, construction, operation, or maintenance that materially affects the potential for leaks or spills of spent pulping liquor, soap, or turpentine from the immediate process areas.

(i) Monitoring, corrective action, and reporting requirements. (1) Each mill subject to this section must conduct daily monitoring of the influent to the wastewater treatment system in accordance with the procedures described in paragraph (h)(2) of this section for the purpose of detecting leaks and spills, tracking the effectiveness of the BMPs, and detecting trends in spent pulping liquor losses.

(2) Whenever monitoring results exceed the *lower action level* for the period of time specified in the BMP Plan, the mill must conduct an investigation to determine the cause of such exceedance. Whenever monitoring results exceed the *upper action level* for the period of time specified in the BMP Plan, the mill must complete corrective action to bring the wastewater treatment system influent mass loading below the *lower action level* as soon as practicable.

(3) Although exceedances of the action levels will not constitute violations of an NPDES permit or pretreatment standard, failure to take the actions required by paragraph (i)(2) of this section as soon as practicable will be a permit or pretreatment standard violation.

(4) Each mill subject to this section must report to the NPDES permitting or pretreatment control authority the results of the daily monitoring conducted pursuant to paragraph (i)(1) of this section. Such reports must include a summary of the monitoring results, the number and dates of exceedances of the applicable action levels, and brief descriptions of any corrective actions taken to respond to such exceedances. Submission of such reports shall be at the frequency established by the NPDES permitting or pretreatment control authority, but in no case less than once per year.

(j) Compliance deadlines. (1) Existing direct and indirect dischargers. Except as provided in paragraph (j)(2) of this section for new sources, indirect discharging mills subject to this section must meet the deadlines set forth below. Except as provided in paragraph (j)(2) of this section for new sources, NPDES permits must require direct discharging mills subject to this section to meet the deadlines set forth below. If a deadline set forth below has passed at the time the NPDES permit containing the BMP requirement is issued, the NPDES permit must require immediate compliance with such BMP requirement(s).

(i) Prepare BMP Plans and certify to the permitting or pretreatment authority that the BMP Plan has been prepared in accordance with this regulation not later than *[insert date 12 months after date of publication]*;

(ii) Implement all BMPs specified in paragraph (c) of this section that do not require the construction of containment or diversion structures or the installation of monitoring and alarm systems not later than *[insert date 12 months after date of publication]*.

(iii) Establish initial action levels required by paragraph (h)(3) of this section not later than *[insert date 12 months after date of publication]*.

(iv) Commence operation of any new or upgraded continuous, automatic monitoring systems that the mill determines to be necessary under paragraph (c)(3) of this section (other than those associated with construction of containment or diversion structures) not later than *[insert date 24 months after date of publication]*.

(v) Complete construction and commence operation of any spent pulping liquor, collection, containment, diversion, or other facilities, including any associated continuous monitoring systems, necessary to fully implement BMPs specified in paragraph (c) of this section not later than *[insert date 36 months after date of publication]*.

(vi) Establish revised action levels required by paragraph (h)(4) of this section as soon as possible after fully implementing the BMPs specified in paragraph (c) of this section, but not later than *[insert date 45 months after date of publication]*.

(2) New Sources. Upon commencing discharge, new sources subject to this section must implement all of the BMPs specified in paragraph (c) of this section, prepare the BMP Plan required by paragraph (d) of this section, and certify to the permitting or pretreatment authority that the BMP Plan has been prepared in accordance with this regulation as required by paragraph

(f) of this section, except that the action levels required by paragraph (h)(5) of this section must be established not later than 12 months after commencement of discharge, based on six months of monitoring data obtained prior to that date in accordance with the procedures specified in paragraph (h)(2) of this section.